

536.5
D33 r

REMOTE STOR.

[REPRINTED FROM VOL. I. OF "THE DICTIONARY OF APPLIED PHYSICS."]

UNIVERSITY OF ILLINOIS LIBRARY

JUL 26 1922

REALISATION

OF

ABSOLUTE SCALE OF TEMPERATURE¹

I. TEMPERATURE SCALES

§ (1) DEFINITION OF TEMPERATURE. — Notwithstanding the fact that temperature is one of the oldest and most familiar concepts of physics, it is only within comparatively recent times that this concept has been subjected to careful analysis and definition. Kelvin and others have shown² how temperature may be defined in terms of the availability of energy, and the definition made wholly independent of any property of any substance.

This definition may be put in the form

$$\frac{\theta_1}{\theta_2} = \frac{Q_1}{Q_2}$$

in which θ_1 and θ_2 are two different temperatures between which an ideal engine has operated (as, for example, with a Carnot cycle) in converting the quantity of heat $Q_1 - Q_2$ into mechanical work.

§ (2) MEASUREMENT OF TEMPERATURE-

¹ The arabic numbers in parenthesis in the text refer to the Bibliography at the end of the article.

² For full discussion see the article on "Thermodynamics."

MAGNITUDES.—It has been suggested (111) that the expression

$$\theta = \frac{dQ}{dS}$$

where θ is temperature and dS is the infinitesimal change in entropy³ corresponding to the absorption of the heat energy dQ in a reversible process, be made to define temperature as a *derived* or secondary quantity, in terms of energy and entropy as the fundamental concepts. The usual method, however, and the one we shall follow here, is to consider entropy as a derived quantity, and temperature as one of the *fundamental* concepts.

Temperature differs from energy, length, mass, etc., in being an "intensive" magnitude, whereas energy, length, and mass are "extensive" magnitudes, i.e. are additive. To put our energy-definition of temperature into usable form, therefore, it becomes necessary to associate it with a continuous energy-change in some form of matter when that form of matter is subjected to change of temperature from one arbitrary standard value to another

³ For a definition and discussion of entropy see "Thermodynamics," § (24).

mac

14 Dec 22 div 9.

arbitrary standard value. The measurement is not influenced by the form of matter chosen.

§ (3) ADOPTION OF NUMERICAL UNIT. THE THERMODYNAMIC SCALE.—The first problem is the finding of standard reproducible temperatures for adoption as standard values. A fixed and reproducible temperature is determined only if we have equilibrium¹ among $n+2$ phases in a system of n components; or among $n+1$ phases if the pressure is fixed; or among n phases if the pressure and one concentration are fixed, etc. From the immense number of such possible systems, each having a fixed temperature, there have been selected, by common consent, two systems for use in the definition of the unit of temperature; they are as follows:

(i.) The one-component system, water. Pressure: 1 standard atmosphere. Phases in equilibrium: liquid and crystalline.

(ii.) The one-component system, water. Pressure: 1 standard atmosphere. Phases in equilibrium: liquid and vapour.

The fixed temperature of system (i.) is usually called "the ice-point," and that of system (ii.) "the steam-point."

The difference between the temperatures (i.) and (ii.) is, by general agreement, called 100° , and the magnitude of a degree of temperature is thereby defined.

It should be noted at this point that the arbitrary assignment of any number, such as 0° , to temperature (i.) is not within the scope of the definition. The temperature of point (i.) is a "constant of nature" to be experimentally determined. If this temperature be called θ_0 , then the temperature (ii.) is $\theta_0 + 100$.

This scale of temperature may be called the *absolute thermodynamic scale* or the *Kelvin thermodynamic scale*. Temperatures expressed in terms of this scale are frequently indicated by the letter K or the abbreviation *Abs.* Meteorologists use *a*.

§ (4) EXPERIMENTAL REALISATION. THE CENTIGRADE THERMODYNAMIC SCALE.—Having our concept of a scale of temperature thus satisfactorily defined in terms of the laws of energy, and our unit of measurement defined by the adoption of the melting- and boiling-points of water at atmospheric pressure as arbitrary standard temperatures differing by 100° (but without numerical values), we are face to face with the fundamental practical problem of the experimental realisation of the scale. This problem evidently consists in determining (i.) the value of the temperature θ_0 ; (ii.) the variation with temperature of some property of some substance or object which may then be adopted as a working standard.

The determination of the numerical value

¹ See article on "Phase Rule," Vol. IV.

of θ_0 is a matter of some experimental difficulty. Fortunately, the progress of exact thermometry need not wait for this determination, for we can define another scale thus:

$$t_\theta = \theta - \theta_0.$$

This derived scale is called the *centigrade thermodynamic scale*. Temperatures thereon are indicated² by the letter C. The ice-point becomes on this scale exactly 0 by definition.

The experimental determination of the true value of θ_0 will be considered elsewhere.

The second part of our experimental problem, as has been said, consists in selecting a particular property of a particular substance or object as a working standard, and determining the variation of that property with temperature. Logically, it makes no difference what property or what substance is studied, provided the *quantities of energy* involved are determinable.

§ (5) THE IDEAL GAS-THERMOMETER.—Practically, however, the substance chosen has been, almost of necessity, one of the so-called "permanent gases," and the property chosen has been either the pressure or the specific volume of the gas. The experimental apparatus for measuring this pressure or specific volume constitute what is generally known as the "gas-thermometer."

The reason why we turn to these particular substances and properties is found in the simple relation which holds *very nearly* between the pressure, specific volume, and temperature of a "permanent" gas when the temperature is that already defined (Kelvin scale). This relation is expressed in the equation

$$pv = k\theta,$$

in which p is pressure; v , specific volume; θ , temperature; and k a constant. An "ideal gas" may be defined, for thermometric purposes (15), as one which obeys this law at all values of p , v , and θ .

It is important at this point to recall that our initial measurements with the gas-thermometer tell us nothing about whether the gas in question obeys the law $pv = k\theta$ or not. Only measurements of the energy-relations of the gas can give us that information. But since such measurements involve the measurement of temperature, it is evident that the realisation of the temperature scale is logically a process of successive approximations. Practically, the first approximation is sufficient, so nearly do the gases commonly used in gas-thermometers conform to the "ideal" behaviour expressed in the law $pv = k\theta$.

² As ordinarily employed the letter C may indicate almost any scale—mercurial, normal hydrogen, constant-pressure nitrogen, etc.—which approximates to the centigrade thermodynamic scale. Its current use is not as precise as it should be.

§ (6) THE "IDEAL-GAS" THERMOMETER.—Let us suppose that a series of energy and pressure measurements have enabled us to find a gas which, within our working range and within the limits of accuracy of our observations, conforms exactly to the relation $pv=k\theta$. This gas may then be used, within that working range, as the standard substance of our fundamental thermometer, and we shall have what may be called an "ideal-gas thermometer."

§ (7) THE "PERFECT" GAS-THERMOMETER.—Let us suppose, on the other hand, that no ideal gas has been found as the result of our series of approximations, but that we have succeeded in determining, within our working range, all the deviations of one particular gas from the relation $pv=k\theta$. This gas may then be used, within this range, as the standard substance to define the temperature scale, and our pressure or specific-volume measuring apparatus together with a table of these pressure or volume deviations will constitute what may be called a "perfect gas-thermometer."

§ (8) THE ACTUAL GAS-THERMOMETER.—Historically, neither of the above-mentioned thermometers has been available at any given era in a form possessing the desired precision. Either the margin of error within which a gas could be considered "ideal" was too large, or the margin of possible error in defining a temperature with our imaginary "perfect gas-thermometer" was too large, to be in accord with the known precision of various secondary thermometers.

It has been found expedient, therefore, not only to make the first compromise, already mentioned, of adopting a "centigrade thermodynamic scale" (with ice-point at 0°) in place of the "Kelvin thermodynamic scale," but also to make a second compromise with experimental expediency, and *redefine temperature* in terms of an arbitrarily selected property of some arbitrarily selected gas at an arbitrarily selected initial pressure. This compromise is the more satisfactory the nearer the gas in question comes to being an "ideal gas."

This compromise, it may be noted, is of exactly the same character as those made in defining any working standard or unit (for instance, the electrical units) where *experimental precision* is the primary consideration and logical theoretical exactness is made secondary.

§ (9) THE ABSOLUTE GAS SCALES.—Accordingly, we will define a new temperature, T , by means of the relation

$$pv=k'T, \text{ i.e. } T=\frac{pv}{k'}.$$

It is obvious that this definition, unlike those that have preceded, involves three further

choices, necessarily arbitrary in character and dictated by expediency or experience: (i.) what gas shall be used; (ii.) whether p or v shall be the variable; (iii.) what shall be the initial value of p . Evidently we may have several times as many scales as we have gases.

Certain further assumptions are necessary to give numerical values to any one of these scales; in other words, it is necessary to assign a value to k' . As before (see § (3)), the temperature interval between the ice-point and the steam-point will be called 100° . This will be adopted for all of the gas scales.

§ (10) ABSOLUTE CONSTANT-VOLUME SCALE.—Let a certain gas be selected, at an initial pressure (*i.e.* pressure at the ice-point) represented by p_0 , and let pressure be the property to be measured.

Let p_{100} represent the pressure of the same mass of the gas in the same volume at the steam-point. Let p represent its pressure in the same volume at any other temperature T . Call the ice-point and steam-point on the new scale T_0 and T_{100} respectively.

Then, by the definitions above, v and k' being constant,

$$\frac{T}{T_0} = \frac{p}{p_0} \text{ and } \frac{T}{T_{100}} = \frac{p}{p_{100}},$$

whence

$$T = (T_{100} - T_0) \frac{p}{p_{100} - p_0} = \frac{100p}{p_{100} - p_0}.$$

Another similar "constant-volume" scale may be defined with the same gas, but at some other initial pressure. Still other similar scales may be obtained by substituting other gases.

The scales so defined are called, according to the gas used and according to its initial pressure:

Absolute constant-volume hydrogen scale at initial pressure x .

Absolute constant-volume nitrogen scale at initial pressure x .

Absolute constant-volume air scale at initial pressure x . Etc., etc.

§ (11) ABSOLUTE CONSTANT-PRESSURE SCALE.—Again, let a certain gas be selected, at an initial pressure (at the ice-point) of p_0 , but let *specific volume* be taken as the variable property to be measured.

Let v_{100} represent the specific volume of the gas at the steam-point. Let v represent its specific volume at any other temperature T' . Call the ice-point and the steam-point on the new scale T'_0 and T'_{100} respectively.

Then, by the definitions, p and k' being constant,

$$\frac{T'}{T'_0} = \frac{v}{v_0} \text{ and } \frac{T'}{T'_{100}} = \frac{v}{v_{100}},$$

whence

$$T' = (T'_{100} - T'_0) \frac{v}{v_{100} - v_0} = \frac{100v}{v_{100} - v_0}.$$

Similar "constant-pressure" scales may be defined with the same gas at some other pressure, or with other gases.

These scales are called, according to the gas used and according to its pressure:

Absolute constant-pressure hydrogen scale at pressure x .

Absolute constant-pressure nitrogen scale at pressure x .

Absolute constant-pressure air scale at pressure x . Etc., etc.

It will be observed that the value of T_0 (or T_0') is not the same on any two of these scales, being dependent on the properties of the gas. On one of the constant-volume scales, for instance, the value of T_0 is given by $100p_0/(p_{100}-p_0)$; while on a constant-pressure scale the value of T_0' is $100v_0/(v_{100}-v_0)$. The value of T_0 (or T_0') does not depart by more than 1° , in most cases, from 273° .

§ (12) THE CENTIGRADE GAS SCALES.—A sub-compromise similar to that in paragraph (4) is now in order, again in the interest of experimental precision and convenience, since, as we have just seen, T_0 (or T_0'), the ice-point, has an independent value on each one of the absolute gas scales. This compromise consists in defining a derived scale by the relation

$$t_v = T - T_0 \text{ or } t_p = T' - T_0',$$

thus making the ice-point 0° by definition.

The scales so defined are called, according to (1) the variable, (2) the gas, and (3) the initial pressure:

Centigrade constant-volume hydrogen scale at initial pressure x .

Centigrade constant-pressure hydrogen scale at pressure x .

Centigrade constant-volume nitrogen scale at initial pressure x .

Centigrade constant-pressure air scale at pressure x . Etc., etc.

These scales differ among themselves by amounts which are never of importance industrially, but which are approximately determinable and of considerable significance in exact scientific work, as we shall see later.

§ (13) GAS SCALES IN COMMON USE.—The state of international agreement on temperature scales is not so far advanced as is agreement on standards of length, electrical quantities, etc. A conference between representatives of various national standardising laboratories, to draft an international agreement on temperature scales, had been called for September 1914, but was prevented by the outbreak of war.¹

The only officially recognised international scale is the *centigrade constant-volume hydrogen scale at an initial pressure of 1000 mm. mercury*,

¹ See "Temperature, Practical Scale of."

adopted by the International Committee on Weights and Measures on October 15, 1887, and known as the "normal hydrogen scale" (*échelle thermométrique normale*).

At temperatures below 0° the normal hydrogen scale and the *centigrade constant-volume helium scale at initial pressure of 1000 mm.* have been most used. For very low temperatures it becomes necessary to use a constant-volume helium scale at a much lower initial pressure. For temperatures above 100° the scale which has been in widest use is the *constant-volume nitrogen scale at an initial pressure of about 500 mm. mercury*.

§ (14) INTERCOMPARISON OF THE GAS SCALES.

—There are two ways of comparing the different gas scales with each other, and determining the corrections to be used in translating experimental data from one scale to another.

One way would be to put the two gas-thermometers side by side into a thermostat at uniform temperature and compare their readings, setting the thermostat at various temperatures. Suppose a constant-volume hydrogen thermometer at initial pressure 1000 mm. placed in a thermostat side by side with a constant-volume nitrogen thermometer at initial pressure 500 mm. The pressures might read, say 1183.132 mm. and 591.706 mm. respectively. The temperature of the thermostat is therefore defined by the first thermometer as 50.0012° and by the second as 50.0027° . The correction for translating data from the first scale to the second would be, therefore, $+0.0015^\circ$ at 50° .

This method of direct comparison has been used more frequently at temperatures below 0° than at temperatures above 0° .

The second method is indirect. It consists in determining the departure of each gas, under the given conditions, from the ideal gas relation $pv = k\theta$. It is obvious that from such a set of data the differences between the centigrade-thermodynamic temperature of the thermostat, t_θ , and its various centigrade gas-scale temperatures, $t_{H, p, 1000}$, $t_{H, p, 760}$, $t_{N, v, 500}$, etc., could readily be tabulated, and the difference between any two of the gas scales could be found by subtraction of their centigrade thermodynamic corrections.

This is the method of comparison upon which dependence is now very generally placed, but the data thus far published are in many cases unduly divergent, and afford little ground for confidence that a final solution is within reach until considerably more experimental work has been done.

Intercomparison of the gas scales will be more fully considered in Part III. § (17).

For convenience of reference there is added, in Table 1, a list of the more commonly used scales.

II. FORMS OF GAS-THERMOMETER

§ (15) We have seen that either pressure or specific volume of a given gas may be taken as the property to be used in defining a temperature scale. Three limiting forms of the gas-thermometer for carrying out such measurements may be distinguished, depending upon which of the three quantities—mass, volume, pressure—is permitted to vary. These forms are:

(i.) The thermometer with fixed mass of gas, fixed volume, and variable pressure; commonly known as the “constant-volume gas-thermometer.”

frequently called the “dead space” or “unheated space.”¹

The essential parts of a gas-thermometer of type (ii.) are: (a) the bulb; (b) the manometer; (c) the arrangements for measuring the amount of gas withdrawn from the bulb.

Any actual gas-thermometer is to a certain degree a combination of two or more of the limiting types. The volume of the containing vessel is never constant with changing temperature, but varies on account of thermal and elastic expansion. The mass of gas which is at the temperature θ is not always constant, for changing pressure forces some of it into or out of the tube that connects the

TABLE I
EXAMPLES OF TEMPERATURE SCALES

	Abbreviation.	Symbol.	Ice-point.
Absolute thermodynamic scale or Kelvin thermodynamic scale	K	θ	$273.10 \pm 0.05^*$
Centigrade thermodynamic scale	C	t_θ	0^\dagger
Absolute constant-volume hydrogen scale at initial pressure 1000 mm.	..	$T_{H, 1000}, T_H$ or T	$273.03 \pm 0.05^*$
Absolute constant-volume helium scale at initial pressure 1000 mm.	..	$T_{He, 1000}$ or T_{He}	$273.11 \pm 0.03^*$
Absolute constant-pressure nitrogen scale at pressure 1000 mm.	..	$T'_{N, 1000}$	$272.24 \pm 0.05^*$
Absolute constant-volume nitrogen scale at initial pressure 500 mm.	..	$T_{N, 500}$ or T_N	$272.63 \pm 0.05^*$
Centigrade constant-volume hydrogen scale at initial pressure 1000 mm., or “normal hydrogen scale”	..	$t_{H, v, 1000}, t_H$ or t	0^\dagger
Centigrade constant-volume nitrogen scale at initial pressure 500 mm.	..	$t_{N, v, 500}$	0^\dagger
Centigrade constant-pressure nitrogen scale at pressure 1000 mm.	..	$t_{N, p, 1000}$	0^\dagger
Centigrade constant-volume helium scale at initial pressure 1000 mm. (proposed “international helium scale”)	..	$t_{He, v, 1000}$ or t_{He}	0^\dagger

* Experimentally determined.

† Defined.

(ii.) The thermometer with fixed pressure and fixed volume, but variable mass of gas; commonly known as the “constant-pressure gas-thermometer.”

(iii.) The thermometer with fixed mass of gas, fixed pressure, and variable volume.

The property measured in type (i.) is the pressure of the gas; in types (ii.) and (iii.) the specific volume of the gas. As already mentioned, slightly different scales result from using the gas at different initial pressures.

For reasons of experimental convenience type (iii.) has never been used, because of the difficulty of measuring a variable volume at temperatures considerably different from atmospheric.

The essential parts of a gas-thermometer of type (i.) are: (a) the containing vessel or “bulb”; (b) the manometer; (c) the tube connecting the bulb and the manometer,

containing vessel with the manometer. The pressure is never constant with changing temperature, on account of the necessity of adjustment, and must always be measured to ascertain its deviations from constancy. All these variations, however, are of the nature of corrections seldom exceeding 1 per cent, so that it remains true that any actual gas-thermometer conforms fairly closely to one or other of the limiting types.

§ (16) RELATIVE ADVANTAGES OF THE TWO PRINCIPAL TYPES.—If we were dealing with an ideal gas there would be no theoretical advantage in any one of these three limiting types of gas-thermometer over the other two, and the choice would become solely a matter of experimental convenience and precision.

From this standpoint type (i.), the “constant-volume thermometer,” is generally admitted to have the advantage, and has been

¹ “Espace nuisible,” “schädlicher Raum.”

preferred by most investigators. Its manipulation is simple, requiring no transfer of gas or measurement of the amount transferred.

In dealing with a gas which is not "ideal" we have to consider not only experimental convenience and precision in the gas-thermometer itself, but the state of the science as regards the accuracy of our knowledge of the deviations of the gas from the law $p v = k \theta$, for our goal is first the centigrade thermodynamic scale and ultimately the Kelvin thermodynamic scale, and our compromise on the various centigrade gas scales for reasons of experimental precision is to be regarded as only a passing stage in thermometric progress. From this standpoint type (ii.), the "constant-pressure thermometer," has been shown by Buckingham (14) to have a slight advantage at the moment, for the corrections necessary to translate readings on any of the constant-pressure gas scales into temperatures on the centigrade thermodynamic scale are a little more accurately known than the corresponding corrections for the constant-volume scales.

III. BASIC EXPERIMENTAL RESULTS WITH GAS-THERMOMETERS

§ (17) EXPERIMENTAL RANGES.—In dealing with the results of experimental investigation in gas thermometry it will frequently be convenient to recognise that the subject naturally divides itself, both historically and practically, according to the kind and extent of experimental facilities and experience necessary to realise different portions of the temperature scale. The most convenient range for experimental work is that from 0° to 100° C., and this range was the first to be studied in detail. From 0° downward a special kind of technique and experience is required, while from 100° upward a rather different, but again special, kind of technique and experience has had to be developed. The range above 100° may again be divided, on similar grounds, into the range 100° - 500° , within which most of the ordinary materials of construction are available for experimental work; and the range above 500° , where available construction materials begin, one by one, to fail as the temperature rises, either through oxidation, mechanical weakness, or actual fusion.

§ (18) PRESSURE AND VOLUME COEFFICIENTS OF GASES.—As we have seen (§ (12)), the centigrade gas scales are defined in such a way that the temperature 0° is arbitrarily assigned to the ice-point under one atmosphere pressure, whence the temperature 100° becomes assigned to the steam-point under one atmosphere, by virtue of the definition of the unit of measurement in § (3).

These two fixed temperatures therefore become fundamental reference points for any type of gas thermometer, and all of its tempera-

ture indications are based upon measurements of pressure or volume at these two points.

We have seen that for each of the absolute constant-volume gas scales there is a value of T_0 , the ice-point, given by the relation

$$T_0 = \frac{100 p_0}{p_{100} - p_0};$$

also that any other temperature, T , is defined by

$$T = T_0 \frac{p}{p_0},$$

and that the corresponding centigrade temperature is defined by

$$t_v = T - T_0.$$

The constant $(p_{100} - p_0)/100 p_0 = 1/T_0$ is called the "pressure-coefficient" of the gas at the initial pressure stated, and is usually represented by the symbol β .

Correspondingly, for each of the absolute "constant-pressure" gas scales there is a value of T'_0 , the ice-point, given by the relation

$$T'_0 = \frac{100 v_0}{v_{100} - v_0};$$

also, any other temperature, T' , is defined by

$$T' = T'_0 \frac{v}{v_0},$$

and the corresponding centigrade temperature is defined by

$$t_p = T' - T'_0.$$

The constant $(v_{100} - v_0)/100 v_0 = 1/T'_0$ is called the "volume-coefficient" of the gas at the pressure stated, and is represented by the symbol α .

Obviously, although it is necessary in a given gas-thermometer to measure p_0 or v_0 , it is not necessary to measure with it β or α , since these are constants of the gas and not of the thermometer.¹

Measurements of β and α for particular gases are listed in Tables 2 and 3.

§ (19) COMPARISON OF THE DIFFERENT GAS SCALES. DIRECT METHOD.—Since necessity or convenience has brought about the use of several different gas scales, it becomes of importance to know the corrections by which readings in any one of these can be reduced to a common standard, such as the normal hydrogen scale.

The direct method of determining these corrections, as has been said, is to put the two thermometers side by side into a thermostat, and compare the temperatures as defined by each of the two thermometers; or to measure a given temperature (controlled by a secondary thermometer or reproduced by a melting-point, for example) first with the one gas-thermometer and then with the other.

¹ For a fuller discussion the reader is referred to the article on "Thermodynamics."

TABLE 2
 PRESSURE-COEFFICIENTS OF VARIOUS THERMOMETRIC GASES. VALUES OF $10^6\beta$

$p_0 = 1000$ mm.	760 mm.	500 mm.	Author, Date, and References.
<i>Hydrogen.</i>			
3662.5	Chappuis (21), 1888.
3662.7	Onnes and Boudin (88), 1900.
..	3662.6	3662.7	Travers and Jaquerod (114), 1903.
3663.0	} Chappuis (22), 1907.
3662.2	
..	..	3661.8	Holborn and Henning (64), 1911.
<i>Helium.</i>			
..	3662.6	3662.3	Travers and Jaquerod (114), 1903.
3661.3	} Onnes (87), 1907.
3661.6	
..	..	3661.8	Holborn and Henning (64), 1911.
<i>Nitrogen.</i>			
3674.7	Chappuis (21), 1888.
..	3671.4	3668.1	} Chappuis and Harker (24), 1902.
..	..	3667.8	
3673	3670	3667.5	Day and Clement (34), 1908.
..	3671.2	3667.9	} Holborn and Henning (64), 1911.
..	3670.2	3666.4	
..	..	3668.5	Day and Sosman (35), 1912.
..	..	3669.1	Chappuis (23), 1917.
<i>Air.</i>			
3674.4	Chappuis (22), 1907.
<i>Oxygen.</i>			
..	..	3671.7	Makower and Noble (80), 1903
<i>Carbon Dioxide.</i>			
3724.8	Chappuis (21), 1888.
3726.3	3712.3	3697.1	„ (22), 1907.

 TABLE 3
 VOLUME-COEFFICIENTS OF VARIOUS THERMOMETRIC GASES. VALUES OF $10^6\alpha$

$p = 1000$ mm.	760 mm.	500 mm.	Author.
<i>Hydrogen.</i>			
3660.0	Chappuis (22), 1907.
<i>Nitrogen.</i>			
3673.1	} Chappuis (22), 1907.
3673.2	
..	3669.8	3666.8	Eumorfopoulos (48), 1914.
<i>Air.</i>			
3672.8	Chappuis (22), 1907.
..	3670.8	..	Eumorfopoulos (47), 1908.
<i>Carbon Dioxide.</i>			
3741.0	3723.7	3706.1	Chappuis (22), 1907.

(i.) *Range 0° to 100°*.—In the range 0°–100° Chappuis (21) made in 1888 a direct comparison of the kind indicated, between constant-volume hydrogen, nitrogen, and carbon dioxide gas-thermometers. In 1907 (22) he extended the comparison to constant-pressure thermometers of the same three gases. He found the following differences (shown in Table 4) between the normal hydrogen scale (t_H) and the other scales.

TABLE 4
VALUES OF $t_H - t$ ACCORDING TO CHAPPUIS' COMPARISONS

	At 20°.	At 40°.
$t_H - t_{N, v, 1000}$ {	-0.010° (1888) -0.005 (1907)	-0.011° (1888) -0.008 (1907)
$t_H - t_{N, p, 1000}$	-0.021	-0.020
$t_H - t_{H, p, 1000}$ {	-0.003 0.000 *	+0.004 -0.001 *
$t_H - t_{CO_2, v, 500}$	+0.002	+0.010
$t_H - t_{CO_2, v, 1000}$	-0.039	-0.039
$t_H - t_{CO_2, p, 500}$	-0.027	-0.026
$t_H - t_{CO_2, p, 1000}$	-0.102	-0.133

* Compared with 1888 results at constant-volume through mercury thermometers.

Since the limit of reproducibility of Chappuis' results was about 0.005°, differences of less than that amount are of little significance. To this degree of exactness, therefore, the constant-volume and constant-pressure hydrogen scales are seen to be in exact agreement at 20° and 40°, while the other gas scales show measurable deviations from the normal hydrogen scale at those temperatures.

(ii.) *Range -273° to 0°*.—Olszewski (86) in 1896 compared constant-volume hydrogen and helium thermometers at -183° to -211°, and found that they agreed within 0.1° in that range.

In the same year Holborn and Wien (68) compared constant-volume hydrogen and air thermometers, and found that the air thermometer indicated a temperature 0.5° to 0.7° lower than the hydrogen at liquid air temperatures. Holborn confirmed this observation in 1901, finding a difference of $0.50^\circ \pm 0.06^\circ$ between nitrogen and hydrogen thermometers at initial pressure 1000 mm.

Travers and Fox (112) observed a large effect of the value of the initial pressure on the deviations of the constant-volume oxygen thermometer, which reads lower than helium by an amount which varies with p_0 , and is of the order of magnitude of 0.4° to 1.5°.

Travers, Senter, and Jaquerod (114) in

1903 compared constant-volume hydrogen and helium thermometers at initial pressures of 845–975 mm., through the intermediary measurement of the vapour pressures of oxygen and hydrogen. They found the hydrogen temperatures to be 0.10° lower than the helium in the neighbourhood of -190°, and 0.19° lower at -253°.

Kamerlingh Onnes and Holst (99) also made a careful comparison between the constant-volume hydrogen and helium thermometers, using a platinum-resistance control, at temperatures from 0° to -258°. The differences between the two did not exceed 0.06° down to -100°, and they may be considered as defining the same temperature within that range to an accuracy of 0.02°. At -258° the hydrogen thermometer yielded a temperature 0.12° to 0.15° lower than the helium.

(iii.) *Range 100° to 500°*.—Holborn and Henning's investigations (64) in 1911 constitute a comparison of the constant-volume hydrogen, helium, and nitrogen scales at initial pressures of 620–630 mm., using two platinum-resistance thermometers as intermediaries. In terms of one of these two the hydrogen and helium scales agreed exactly, to 0.01°, at 450°; in terms of the other, the helium-scale temperature was 0.07° lower than the hydrogen. The nitrogen scale was 0.11° to 0.12° lower than the hydrogen at 450°. The results indicate that the hydrogen and helium scales are in agreement at 450° within 0.05° or less, while the constant-volume nitrogen scale at initial pressure of about 600 mm. requires a correction of about 0.1° to convert its readings to the normal hydrogen scale.

Eumorfopoulos' determinations of the boiling-point of sulphur (48) in 1914, likewise, constitute a comparison of the constant-pressure nitrogen scale at pressure 792 mm. with the similar scale at 415 mm. The difference between the two was found to be 0.23° at 444.5°. Hence, on the fairly exact assumption that the correction is proportional to the pressure, the correction to convert the constant-pressure nitrogen scale at 1000 mm. to the thermodynamic scale is $+0.60^\circ \pm 0.05^\circ$.

(iv.) *Range above 500°*.—The only exact comparison of gas-thermometers in this range is that by Jaquerod and Perrot (72). Using a bulb of fused silica, they determined the melting-point of gold on the constant-volume nitrogen, oxygen, air, carbon dioxide, and carbon monoxide scales at initial pressures of 182–252 mm.

Although some of their errors, particularly that due to non-uniformity of temperature, were abnormally large, nevertheless the fact that all of the gases were used under identical conditions makes the work a fairly reliable comparison between scales, even though their

absolute value for the melting-point of gold is open to question.

Expressed in terms of corrections to convert readings on one of the gas scales to readings on the constant-volume nitrogen scale at initial pressure of about 250 mm., their results were :

$$t_{\text{N}, v, 250} - t_{\text{air}, v, 250} = 0.0^{\circ},$$

$$t_{\text{N}, v, 250} - t_{\text{CO}_2, v, 250} = +0.9^{\circ},$$

$$t_{\text{N}, v, 250} - t_{\text{O}, v, 250} = +0.4^{\circ},$$

$$t_{\text{N}, v, 250} - t_{\text{CO}, v, 250} = +0.15^{\circ}.$$

§ (20) COMPARISON OF GAS SCALES BY THE INDIRECT METHOD, AND DIFFERENCES BETWEEN GAS SCALES AND THE CENTIGRADE THERMODYNAMIC SCALE.—The indirect method of comparison consists, as has been said, in calculating from existing energy-data of the thermometric gases the corrections necessary to reduce temperatures on one of the centi-

corrections in the intermediate range may be gained from Table 5, which compares the differences between centigrade thermodynamic temperature, t_{θ} , and gas-scale temperatures, calculated for the temperature 50° by some of the authors quoted.

It will be seen that the *normal hydrogen* scale, between 0° and 100° , is experimentally very nearly indistinguishable from the centigrade thermodynamic scale. To a lesser degree of certainty the same is true of the *constant-pressure hydrogen* scale from 0° to 100° , as is evident from both Table 4 and Table 5. The corrections for the *constant-pressure nitrogen* scale in this range are in fairly satisfactory agreement with Chappuis' directly determined differences (see Table 4). The *constant-volume nitrogen* correction is more uncertain; Buckingham's figure is much smaller than the others and smaller than the results of direct comparison; on the other

TABLE 5
COMPARISON OF GAS-SCALE CORRECTIONS AT 50° , IN THOUSANDTHS OF A DEGREE

	Rose-Innes.	Callendar (I.).	Callendar (II.).	Berthelot.	Buckingham (I.).	Buckingham (II.).	Onnes and Braak.	Hoxton.	Keyes.
$t_{\theta} - t_{\text{H}, v, 1000}$..	- 1.3	- 0.6	- 0.5	- 3.2	..	- 2.0
$t_{\theta} - t_{\text{N}, v, 1000}$	- 5.9	- 8.6	- 1.4
$t_{\theta} - t_{\text{H}, p, 1000}$	- 3.3	- 3.5	- 1.8	- 1.1	- 3.9	- 3.4
$t_{\theta} - t_{\text{N}, p, 1000}$	- 28.9	- 22.6*	- 26.0	- 24.0	- 20.9	- 23.8	- 18.0

* Calculated for air.

grade gas scales to temperatures on another centigrade gas scale or on the centigrade thermodynamic scale. Tables of such corrections have been compiled by Rose-Innes (109), Callendar (17), D. Berthelot (13), and Buckingham (14). Kamerlingh Onnes (87) and Braak (89, 90, 91) calculated the corrections to the constant-volume helium and hydrogen scales at temperatures below 0° . Hoxton (69) calculated corrections for the constant-volume air scale from his experiments on the Joule-Thompson effect. Keyes (75) recomputed the nitrogen corrections on the basis of his new equation of state, which receives considerable support from experimental data.

Limitations of space forbid any extended discussion in this article of the derivation of these corrections.¹ We will confine our attention to a brief indication of the present status of our knowledge of these corrections in relation to experimental gas-thermometry.

(i.) *Range 0° to 100° .*—The scales all coincide, by definition, at 0° and 100° . Some idea of the state of our knowledge of the inter-scale

hand, according to Keyes' equation, the constant-volume nitrogen correction is zero.

(ii.) *Range -273° to 0° .*—Table 6 gives a comparison, similar to that in a preceding paragraph, at the temperature -100° .

The agreement among the different estimates at -100° is very poor. Onnes and Braak's value for the *normal hydrogen* scale is undoubtedly the best, being based on experimentally determined isotherms at low temperatures. Onnes's data on the *constant-volume helium* scale show that it coincides with the thermodynamic scale within 0.01° at -100° , and has a positive correction of not over 0.03° at -250° . The differences between hydrogen and helium are satisfactorily checked by the direct comparisons (see an earlier paragraph).

(iii.) *Range 100° to 500° .*—As before, the estimates of various authors are compared at a single temperature, in this case 400° . (See Table 7.) From Table 7 it is evident that we know very little more of the magnitude of the *constant-volume* hydrogen and nitrogen corrections than we did seventy years ago, when Regnault concluded from his comparisons that the constant-volume air scale needed no

¹ For fuller discussion see the article on "Thermodynamics."

correction. Even Holborn and Henning's direct comparison (see a preceding paragraph) leaves the matter somewhat in doubt.

much better known than the constant-volume corrections. Jaquerod and Perrot's direct comparisons (see a preceding paragraph) are

TABLE 6
COMPARISON OF GAS-SCALE CORRECTIONS AT -100° , IN THOUSANDTHS OF A DEGREE

	Callendar (I.).	Callendar (II.).	Berthelot.	Buckingham (I.).	Buckingham (II.).	Onnes.
$t_{\theta} - t_{H, v, 1000}$	+20	+ 5	+ 8	+ 32	..	+18.7
$t_{\theta} - t_{N, v, 1000}$..	+ 80	+125	- 59
$t_{\theta} - t_{H, p, 1000}$	+66	+ 29	+ 21	+ 46
$t_{\theta} - t_{N, p, 1000}$..	+437	+469	+326	+348	..
$t_{\theta} - t_{He, v, 1000}$	$\left\{ \begin{array}{l} + 3.4 \\ - 6.0 \end{array} \right.$

The constant-pressure hydrogen scale is subject to a positive correction of about 0.1° , while the constant-pressure nitrogen correction is relatively the best known of all, amounting to about $+0.45^{\circ}$ at 400° for a thermometer

of no assistance as regards corrections to the thermodynamic scale.

§ (21) DETERMINATION OF θ_0 .—The numerical value for θ_0 , the ice-point on the Kelvin thermodynamic scale, is one of the basic data

TABLE 7
COMPARISON OF GAS-SCALE CORRECTIONS AT 400° , IN THOUSANDTHS OF A DEGREE

	Callendar (I.).	Callendar (II.).	Berthelot.	Buckingham (I.).	Buckingham (II.).	Keyes.
$t_{\theta} - t_{H, v, 1000}$	+ 12	+ 99
$t_{\theta} - t_{N, v, 1000}$	+194	+139	..	0
$t_{\theta} - t_{H, p, 1000}$	+68	+38	+ 21	+110	+ 68	..
$t_{\theta} - t_{N, p, 1000}$..	+550	+457	+433	+456	+436

at pressure 1000 mm. Eumorfopoulos' (51) direct determination of this correction as $0.60 \pm 0.05^{\circ}$ at 450° furnishes confirmation that the estimates are correct within 0.1° .

(iv.) Range above 500° .—In this range no one has ventured to calculate the differences

of thermometry. While its determination is a fundamental thermometric problem, and forms logically a part of the present article, the problem will be found fully discussed elsewhere in this dictionary.¹ The most reliable estimates vary from 273.08° to 273.14°

TABLE 8
COMPARISON OF GAS-SCALE CORRECTIONS AT 1000°

	Callendar (II.).	Berthelot.	Buckingham (I.).	Buckingham (II.).	Keyes.
$t_{\theta} - t_{N, v, 1000}$	+0.646°	+0.77°	+0.734°	..	0
$t_{\theta} - t_{N, p, 1000}$	+2.047	+1.654	+1.706	+1.721	+1.72

between the scales for any except the constant-volume and constant-pressure nitrogen thermometers at initial pressure 1000 mm. These are shown in Table 8.

In this range, as in the range 100° - 500° , the constant-pressure nitrogen corrections are

and it may be conservatively placed at the value $273.1^{\circ} \pm 0.05^{\circ}$.

§ (22) SUMMARY FOR SECTION III.—Centigrade thermodynamic temperatures can now be measured with several different types of

¹ See article on "Thermodynamics."

gas-thermometer, with an accuracy which is conservatively estimated to be as follows :

At -250°	0.05°	At 200°	0.05°
At -100°	0.02°	At 400°	0.1°
At 0°	0.003°	At 1000°	1°
At 50°	0.006°	At 1500°	2°
At 100°	0.01°		

IV. MEANS OF COMPARISON OF GAS-THERMOMETERS WITH SECONDARY STANDARDS

§ (23) SECONDARY STANDARDS.—A gas-thermometer occupies so much space that it is seldom convenient for use in the direct measurement of temperature. For this reason the experimental realisation of the temperature scale and its translation into terms and measures of convenient application requires a further step, namely, the comparison of gas-thermometers with secondary standards available for general use.

Secondary standards may be classed as of three kinds :

(i.) Reproducible fixed temperatures (melting-points, boiling-points, etc.).

(ii.) Independent thermal properties of substances (vapour-pressure, index of refraction, etc.).

(iii.) Combination of fixed temperatures with a thermal property (resistance thermometer combined with ice, steam, and sulphur points, etc.).

The expression "thermal property" is used here in a broad sense to include any property which varies with temperature and at the same time can be measured with precision.

§ (24) FIXED TEMPERATURES.—In accordance with the Phase Rule,¹ the temperature of a system is fixed if the pressure and the necessary number of concentrations are specified so that in a system of n components

$$P + F = n + 2,$$

where P is the number of phases present and F the number of variables that have been specified.

For instance, take a one-component system such as pure water ; the specifications that the pressure shall be one atmosphere and that the two phases, liquid water and ice, shall be present, determines that this system shall have a fixed and reproducible temperature. Or take the 2-component system—water and sodium chloride ; the specifications that ice and solution shall be present, that the pressure shall be one atmosphere, and that the solution shall have a concentration of 10 parts salt to 90 parts water, again fixes a reproducible temperature. So also does the specification of the three phases, ice, salt, and solution, and a pressure of one atmosphere ; or the specification of the three phases, salt, solution, and vapour,

¹ See "Phase Rule," § (6), Vol. IV.

and a pressure of one atmosphere (boiling-point of the saturated solution).

The temperature of any such system may be measured with a gas-thermometer, and this fixed-temperature system then becomes available either for the direct indication of temperature or for the standardisation of any kind of secondary thermometer.

Customary practice in gas-thermometric work has quite needlessly restricted these fixed-temperature points to one-component systems—to the melting- and boiling-points of pure substances, usually elements.

The gas-thermometer need not be directly immersed in the fixed-temperature system. Many kinds of transferring devices may be used, such, for example, as a thermo-element. The thermo-element is immersed in the fixed-temperature system, say a melting metal, and its E.M.F. is read. Thermo-element and gas-thermometer are then placed side by side in a thermostat whose temperature is regulated until the thermo-element again gives the same E.M.F. A gas-thermometer reading then gives the desired temperature of the fixed point. There need be no sacrifice of accuracy in making the comparison in this way, for the sensitiveness of the thermo-element can easily be made equal to or greater than that of the gas-thermometer by multiplying junctions.

There are two considerations, either of which may dictate the choice of an indirect or transfer method, such as that described above, rather than the direct immersion method. In the first place, uniformity of temperature must be secured over the entire volume of the gas-thermometer bulb, and this frequently calls for the use of a secondary or auxiliary thermometric device of small volume, with which to explore the distribution of temperature. Chappuis' bulb, for example, was over a metre long. In a comparison of this character in which the dimensions of the two measuring instruments differ so extremely a considerable burden is placed on the thermostat to guarantee the constancy of temperature over so large an area with the full precision expected.

Or, to view the problem from a somewhat different angle, the thermostat may fulfil all expectations, but the metal bath or other fixed temperature system be too small or too uncertain in its performance to ensure the expected constancy of temperature over the entire volume of a large gas-thermometer bulb. In this case obviously the transfer method will yield better results than the direct method.

§ (25) THERMAL PROPERTIES.—Any property of a substance which varies with temperature in such a way that it can be measured with accuracy and precision may be made the subject of comparison with a gas-thermometer. The measurements of the property so obtained

may then be stated in terms of a centigrade gas scale or one of the thermodynamic scales, either by means of a table of data, or a graph, or a mathematical formula, and may thus become a secondary standard for the direct measurement of temperature.

This method presupposes that the substance in question can be obtained of such constant and reproducible composition and structure that the thermal property in question is reproducible with a precision equal to that with which the comparison with the gas-thermometer was made. This is a requirement which is difficult to meet in the case of some properties, but is easily met in others.

Some of the properties that have been compared with gas-thermometers with a view to their independent use in secondary thermometry are: the vapour pressure of a pure liquid, the index of refraction of a gas, the specific heat capacity of a solid, and (most important of all) the wave-length and intensity of the radiation from solid bodies.

§ (26) COMBINATION OF FIXED TEMPERATURES WITH A THERMAL PROPERTY.—This method has been the one most commonly used for the realisation of gas-thermometer scales in the form of secondary standards. We may consider that what is really measured and certified to in this case by the gas-thermometer (in addition to the fixed temperatures themselves) is the *manner of variation* of the property in question. It is this manner of variation that is reproducible, not the absolute measure of the property itself.

Take, for example, the electrical conductivity of a particular metal. Electrical conductivity is so sensitive to small amounts of impurities in the metal that it cannot be considered sufficiently reproducible to be an independent secondary standard. But conductivity (or resistance) measurements on a particular sample, in conjunction with gas-thermometer measurements of temperature, may show that the resistance of that sample varies *continuously and reproducibly*, and that it can be represented within the limits of precision of the gas-thermometer by means of a mathematical formula containing as constants the resistance of the sample, say, at three fixed temperatures, whose value is independently known by other gas-thermometer measurements.

If this result is repeatedly obtained on various samples, it is reasonable to assume that any other sample, whose resistance does not vary greatly from those investigated, will likewise have a resistance which varies continuously and reproducibly and can be represented by a similar formula containing as constants the resistance at the selected fixed temperatures.

It will be recognised that measurements of

this kind form the basis of the widespread and successful use of the platinum-resistance thermometer and the metal-alloy thermocouple—two very common kinds of secondary thermometer.

V. COMPARISON OF GAS-THERMOMETERS WITH SECONDARY STANDARDS IN THE RANGE 0° TO 100°

§ (27) FIXED TEMPERATURES.—The numerical values of the temperature of the melting-point of ice and the boiling-point of water are fixed by definition. The question of their reproducibility and precision are considered elsewhere.¹

No fixed temperature within the range 0° to 100° has been made the subject of direct gas-thermometer evaluation.

The temperature of the system $[\text{Na}_2\text{SO}_4 : \text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} : \text{solution}]$, under one atmosphere pressure, in the two-component system [sodium sulphate : water], has been proposed by Richards (105) as a fixed point in this part of the scale. Its temperature was accurately determined by Richards and Wells (106) by means of mercury thermometers calibrated against the standards of the International Bureau, and the determination may therefore be taken as an indirect determination in terms of the normal hydrogen scale. The temperature thus determined was 32.383° . A similar comparison was made by Dickinson and Mueller (43), using platinum-resistance thermometers which had been compared with mercurial standards checked by the International Bureau, and which were believed to represent the hydrogen scale within 0.002° , their figure for the point is 32.384° . The close agreement of these two is good evidence of the reproducibility of the point.

Similar determinations of the temperature of $[\text{MnCl}_2 \cdot 4\text{H}_2\text{O} : \text{MnCl}_2 \cdot 2\text{H}_2\text{O} : \text{solution}]$, at 58.089° , have been made by Richards and Wrede (108); and of the temperature of $[\text{NaBr} : \text{NaBr} \cdot 2\text{H}_2\text{O} : \text{solution}]$, at 50.674° , by Richards and Wells (107). The NaBr point has the disadvantage that the salt is not easily obtained in a sufficiently pure state for exact work.

§ (28) THERMAL PROPERTIES.—No independent thermal property, which could be depended upon for the measurement of temperature without the aid of standardisation at fixed points, has been made the subject of gas-thermometer comparison in the range 0° to 100° .

§ (29) COMBINED THERMAL PROPERTIES AND FIXED TEMPERATURES. (i.) *Expansion of Mercury in Glass*.—The differential cubical expansion of mercury in a particular type of hard glass is a property capable of fairly exact reproduction, with the aid of two fixed

¹ See article on "Thermometry."

temperatures. The use of this property in "mercurial thermometry" is made the subject of a special article in this dictionary and need not be referred to at length here.

The comparison of this property with the constant-volume hydrogen thermometer has been the subject of some of the most exact work on record in gas-thermometry, namely, that of Chappuis (21).

Chappuis used a bulb of platinum-iridium alloy, having a capacity of about 1 litre, and filled with pure hydrogen at an initial pressure at 0° of about 1000 mm. mercury. This was immersed in a thermostat with four standard mercury-in-hard-glass thermometers of the International Bureau, Nos. 4428, 4429, 4430, and 4431. The true temperatures of these thermometers were then determined by the pressure of the hydrogen at about 5°, 10°, 15°, 20°, 25°, 30°, 35°, 40°, 45°, 50°, 61°, and 78°, and the corrections necessary to convert their scale-readings into true temperatures were tabulated.

These four thermometers thus became the custodians, so to speak, of the international temperature scale from 0° to 100°, and all other standard thermometers in the world's various national bureaus of standards have been calibrated by comparison with these four.

(ii.) *Electrical Resistance of Platinum Wire.*—In 1871 Siemens suggested the use of the electrical resistance of platinum wire as a secondary thermometric standard, but it was not put on a really exact basis until Callendar investigated it and revived the suggestion in 1886.¹ In 1891 he and E. H. Griffiths (19) published a direct comparison between a platinum-resistance thermometer and a constant pressure air thermometer at intervals of 5° over the range 0°-100° C. The two thermometers were placed side by side in an iron tank containing some 75 litres of water which was carefully stirred. The differences between the temperatures, as calculated by Callendar's quadratic formula with $\delta=1.474$ and as given by the constant pressure air thermometer, were of the order of 0.01°; this value of δ was not, however, obtained by direct calibration at the sulphur point. The Kew Observatory authorities then took up the matter, and after a study of some of the characteristics of platinum-resistance thermometers had been made by Griffiths and others, requested the International Bureau of Weights and Measures to compare several such thermometers with the normal hydrogen scale, then on deposit at the Bureau in the form of eight mercury thermometers, as mentioned in preceding paragraphs of this section.

¹ For further details see the article on "Resistance Thermometers"; also *Phil. Trans. Roy. Soc. A*, 1887, clxxviii.

The plan was agreed to, and comparisons made by Chappuis and Harker (24) were published in 1902. Comparisons were made in the range -23° to 100° between two platinum-resistance thermometers and the standard mercury thermometers. It was found that temperatures interpolated by means of Callendar's quadratic formula based on calibrations at the ice, steam, and sulphur points deviated from the true temperature by about 0.02° or 0.03° at most (depending upon the value assumed for the sulphur boiling-point). The deviations were not, however, haphazard and accidental; the agreement was not wholly satisfactory, and was evidently not so regarded by the authors.

Except for the investigations of Callendar and Griffiths in 1891, and this comparison by Chappuis and Harker, no exact comparison of the platinum-resistance thermometer at temperatures between 0° and 100° has ever been made either directly with a gas-thermometer or indirectly through a single intermediary. The secondary indirect comparisons made by Griffiths (50) in 1893, Waidner and Mallory (124) in 1898, and by Dickinson, Waidner, and Mueller (43, 121) in 1907, however, gave what are probably more precise results than the primary indirect comparison by Chappuis and Harker, or the original direct work of Callendar and Griffiths, and must be considered the real basis for confidence in the platinum-resistance scale between 0° and 100°. Yet none of these comparisons warrants the statement that the resistance thermometer calibrated at ice, steam, and sulphur points is known with certainty to reproduce the normal hydrogen scale within 0.01°.

§ (30) SUMMARY FOR THE RANGE 0° TO 100°.

(i.) *Mercurial and Resistance Thermometry.*—Although the normal hydrogen scale, as represented by a set of *verre dur* thermometers at the International Bureau, is still the only international standard of temperature, it has in recent years been less generally employed in consequence of the increasing use of and confidence in the platinum-resistance thermometer and the demonstrated variability of mercury-in-glass scales (52). Thus the Reichsanstalt (125) has officially announced its abandonment of the gas-thermometer as a fundamental experimental standard, and its adoption of the resistance thermometer (calibrated at ice, steam, and sulphur points, and having certain limiting values² for its constants) as its fundamental temperature scale for purposes of certification, from -39° to +445°.

Confidence in the resistance thermometer

² R_{100}/R_0 must be not less than 1.388 and δ must be not greater than 1.52, when the boiling-point of sulphur is taken as $444.55 + 0.0908 (p - 760) - 0.000047 (p - 760)^2$.

has been bred by its *convenience* and *precision* rather than by its demonstrated agreement with the normal hydrogen scale, for the demonstration in the range 0° to 100° really rests upon two or three relatively indirect comparisons with the aid of mercury thermometers. The second-degree equation for platinum resistance departs so radically from true temperatures below 0° that some departure, even though small, is rather to be expected above 0° . To cut loose completely from the gas-thermometer, therefore, seems to the writers a step backward toward the days of empirical and arbitrary thermometers and thermometric scales, for so little is known either about the fundamental laws of electrical conduction in metals and the effect of impurities thereon, or about the purification and analysis of platinum, that a new and unexpected impurity in platinum supplies could easily introduce much confusion into the thermometric situation. No objection, however, could be made to the adoption of particular platinum-resistance thermometers, deposited at a national standardising laboratory, as secondary standards to replace secondary mercurial standards.

(ii.) *Thermocouples*.—No general equation for any thermocouple, comparable with that for the resistance thermometer, has been developed. Reliance is placed rather upon tables of E.M.F. and temperature (as is done in the case of resistance thermometry below -40°), and the deviations of any particular thermo-element from the standard table are determined by calibration at fixed points.

(iii.) *Fixed Points*.—For those who do not wish to place full reliance either upon the reproducibility of platinum-resistance thermometers calibrated only at ice, steam, and sulphur points, or upon the reproducibility of thermocouples calibrated at ice, steam, and some other higher point, the following fixed points are available as fundamental reproducible standards (though the temperatures ascribed thereto may be changed by further investigation):

Transition temperature $\text{Na}_2\text{SO}_4 : \text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$: solution, $32.384^{\circ}\text{C.} \pm 0.005^{\circ}$.

Transition temperature $\text{MnCl}_2 \cdot 4\text{H}_2\text{O} : \text{MnCl}_2 \cdot 2\text{H}_2\text{O}$: solution, $58.089^{\circ}\text{C.} \pm 0.005^{\circ}$.

VI. COMPARISON OF GAS-THERMOMETERS WITH SECONDARY STANDARDS IN THE RANGE -273° TO 0°C.

At temperatures above 0°C. the gas-thermometer has seldom been used for the direct measurement of temperature, and its rôle has been confined to that of an ultimate standard against which secondary standards were compared. Below 0° , on the other hand, especially in the pioneer work on

the liquefaction of gases, the use of gas-thermometers for the direct measurement of temperature has been the rule rather than the exception.

We shall not undertake here a discussion of all the researches in which gas-thermometers have been used as measuring instruments, but shall confine our attention to a few researches which have a direct bearing on thermometry.

§ (31) *FIXED POINTS*.—The following fixed points have been made the subject of investigation with gas-thermometers with a view particularly to their use as standard thermometric points: melting-point of mercury; sublimation-point of carbon dioxide; boiling-points of oxygen, nitrogen, hydrogen, and helium.

(i.) *Melting-point of Mercury*.—Chappuis (25) in 1894 extended his comparisons of mercury thermometers with the normal hydrogen thermometer down to the freezing-point of mercury, which he thus determined to be -38.80° . Henning (55) placed it at -38.89° , using platinum-resistance thermometers as intermediaries between the mercury and a constant-volume hydrogen thermometer.

(ii.) *Sublimation-point of Carbon Dioxide*.—The temperature of equilibrium between the solid and gaseous phases of carbon dioxide under a pressure of one atmosphere constitutes a fixed point that has been much used in low-temperature research.

Its temperature was placed by Regnault in 1863 at -78.2° ; by Pictet in 1878 at -80° ; by Villard and Jarry in 1895 at -79° ; by Ladenburg and Krügel in 1899 (hydrogen thermometer) at -78.6° .

A more exact determination, with a constant-volume hydrogen thermometer, was made in 1901 by Holborn (60), who placed the temperature at -78.34° for a mixture of alcohol and solid carbon dioxide.

As usually employed, the solid carbon dioxide is mixed with ether or with alcohol in order to obtain uniformity and good contact with the object to be cooled. If no alcohol or ether were dissolved in the solid CO_2 , and if the vapour pressures of these liquids were inappreciable in comparison with one atmosphere, the equilibrium temperature would be unaffected by their presence. Holborn looked into this question particularly, and found that the temperature of pure, dry, solid CO_2 in equilibrium with the gas at one atmosphere is -78.44° , or 0.10° lower than that of the alcohol mixture. This difference was confirmed by Kaspar (74) in 1913.

Henning (55) found by the static method, using platinum-resistance as intermediary between pure CO_2 and the constant-volume hydrogen thermometer, the value -78.52° .

(iii.) *Boiling-point of Oxygen*.—The early determinations (before 1900) by Wroblewski (127), Olszewski, Estreicher (46), Holborn and Wien, and Ladenburg and Krügel gave results, referred to the hydrogen thermometer, which ranged from -181.6 to -182.56° .

Holborn's determination (60) in 1901, using a platinum-resistance thermometer as intermediary from a hydrogen thermometer, gave -182.7° .

Baly's series of experiments (4) on the composition of the gaseous and liquid phases in the system oxygen-nitrogen gave -182.0° on the constant-pressure hydrogen thermometer. Travers believes the results to have been affected by a constant error causing the boiling-point to appear high.

Dewar (41) in 1901 placed the boiling-point at -182.5° , based on direct measurements with constant-volume hydrogen, oxygen, and helium thermometers.

Travers and Fox (112) in 1903 found -183.3° on the scale of a constant-volume oxygen thermometer filled at various initial pressures from 659 to 336 mm. and extrapolated to zero pressure. Travers, Senter, and Jaquero (114) found that liquid oxygen easily superheats as much as 1° , and a reliable boiling-point is obtained only if gas is bubbled through the liquid, or if the point is determined by the static method. Previous measurements might therefore be expected to prove too high. Their final boiling-point (calculated from the published data, which are given directly in absolute gas scale temperatures) is -182.93° by the constant-volume hydrogen thermometer, and -182.83° by the constant-volume helium thermometer, at initial pressures of 845-975 mm. Their determinations were much more exact than any that had preceded.

Another exact determination was made by Kamerlingh Onnes and Braak (92) in 1908, using a platinum-resistance thermometer as intermediary between the boiling oxygen and two constant-volume hydrogen thermometers, which agreed to within 0.04° . The boiling-point is placed at $-183.04 \pm 0.03^{\circ}$ on the normal hydrogen scale, or -182.99° on the centigrade thermodynamic scale.

The most recent determination was by Henning (55) in 1914. Using platinum-resistance thermometers previously compared with a constant-volume hydrogen thermometer, he found the value -183.01° , or -182.97° C. This is in excellent agreement with the preceding value.

(iv.) *Other Fixed Points*.—While a discussion of the boiling-points of nitrogen, hydrogen, and helium, as well as of other low-temperature points which have been suggested as thermometric standards, might properly form a part of this section, they have been fully covered

elsewhere,¹ so that there is no need of duplicating the discussion here. We could only urge that, when these data are being considered from the standpoint of fundamental thermometry, care be taken to distinguish those determinations which are made by direct or indirect comparison with a gas-thermometer from those which are based on secondary standards or secondary fixed points; they should not be indiscriminately lumped together without any indication as to their degree of independence, as is too often done in tables of physical constants.

§ (32) THERMAL PROPERTIES. (i.) *Vapour Pressure of Oxygen*.—Stock and Nielsen (110) in 1906 described a low-temperature thermometer using the vapour pressure of liquid oxygen. The fundamental data for such a thermometer have been provided by the vapour pressure measurements of Onnes and Braak, and Henning, in which temperatures were measured with hydrogen or helium gas-thermometers.

Possessing some of the disadvantages of the gas-thermometer, this vapour-pressure thermometer has not been widely used as a secondary standard, since investigators have usually preferred a secondary thermometer of smaller volume and easier manipulation.

§ (33) COMBINATION OF THERMAL PROPERTIES AND FIXED POINTS. (i.) *Expansion of Mercury in Glass*.—The work of Chappuis on the comparison of mercury thermometers with the hydrogen thermometer, already referred to in the preceding section, covered the range down to -24° C. Four standard thermometers of the International Bureau, Nos. 4479, 4480, 4481, and 4482, are the depositories, so to speak, of this part of the international hydrogen scale. Chappuis' comparisons indicate that other mercury thermometers, made of glass similar to the "verre dur" standards and calibrated at 0° and 100° , can reproduce the normal hydrogen scale between 0° and -24° within 0.01° .

(ii.) *Expansion of Organic Liquids in Glass*.—Holborn (60) compared the petroleum-ether-in-glass thermometer with the nitrogen thermometer to -190° and showed that it could be used for measurements with an accuracy of 1° , but difficulties with the meniscus and the adherence of liquid to the walls have prevented the use of this and similar thermometers (pentane, toluene, alcohol) for accurate thermometry.

(iii.) *Electrical Resistance of Platinum Wire*.—Early investigations by Dewar and Fleming and by Olszewski gave rather variable deviations between the temperature extrapolated by means of the resistance of platinum and the true temperature. This variability was probably due to impure metal.

¹ See article on "Liquefaction of Gases."

Holborn and Wien (68) in 1896 made the first real comparison of the modern platinum-resistance thermometer with a gas-thermometer. Their resistance thermometers were in some cases sealed directly into the glass bulb of the hydrogen thermometer, and, in others, placed alongside the bulb. Comparisons at various temperatures between -18° and -190° indicated that the resistance of the wire could be represented in terms of t by a second-degree equation, with an accuracy of 1° .

Continuing this work in 1901, Holborn showed that the Callendar quadratic formula for a platinum-resistance thermometer, calibrated at the ice, steam, and sulphur points in the usual manner, gives the hydrogen-thermometer temperature at -78° within 0.15° , but is 2° off at -190° .

A similar comparison was made in 1902-1904 by Meilink (81, 82) at Leiden, who showed by measurements at various points between -51° and -210° that the representation of the resistance by a quadratic formula (based only on points below 0°) is only permissible when the desired accuracy is less than 0.2° , and then only down to -197° . For an accuracy of 0.05° down to -197° a cubic formula is required, with calibrations recommended at at least six points.

Finding the gas-thermometer rather cumbersome for their low-temperature work, Travers and Gwyer (113) in 1905 undertook a re-examination of the dependence of platinum resistance on temperature below 0° . As before, the Callendar quadratic formula extrapolation proved to be low both at -78° and -190° . In order to obtain a formula which would yield hydrogen-scale temperatures, the term δ in Callendar's formula, which has a value of about 1.50 above 0° , had to be made 1.84 to 1.90. This variability in the value of δ (equivalent to considerable deviations from a quadratic formula) led them to conclude that the platinum-resistance thermometer could only be used for interpolation between fixed points, and not for extrapolation or for the independent definition of a scale.

An investigation of higher accuracy than had yet been made on the platinum-resistance thermometer at low temperatures was carried out by Kamerlingh Onnes and Clay (94) in 1906. Measuring the temperature at thirteen points between -30° and -259° with a constant-volume hydrogen thermometer whose accuracy was estimated at 0.02° , they found that the resistance of the platinum wire used could be satisfactorily represented only by a cubic formula to which was added also reciprocal powers of the absolute temperature.

As the use of so cumbersome a formula is

impractical, resistance-thermometric practice soon settled down to the use of a standard table of resistances and temperatures, deviations from which might be determined for any particular platinum-resistance thermometer. Kamerlingh Onnes, Braak, and Clay (93) considered in 1907 that the definition of a low temperature by a single determination on a standardised platinum-resistance thermometer has about the same probable error as a determination on the constant-volume hydrogen thermometer, namely, 0.02° or less.

The most recent exact determination of the relation is that by Henning (53, 54) in 1913. He used a constant-volume hydrogen thermometer with glass bulb, at initial pressures of 740 and 822 mm. The Callendar quadratic formula was found to hold down to -40° , but gave temperatures which were 0.08° low at -78° , and rapidly increased its deviation below that temperature. Different platinum thermometers were found to give "platinum temperatures" which differed by as much as 0.50° . Their tabulated indications could, however, be reduced to those of one standard platinum thermometer by means of a "difference formula" (similar to one originally suggested by Nernst), of the form

$$t'_p - t_p = ct_p(t_p - 100),$$

in which t_p is the "platinum temperature" of the standard, and c a constant of the new thermometer. According to Henning's data, comparison of a new thermometer with the standard at one low temperature, such as that of liquid air, determines c with sufficient accuracy.

The difficulty of defining a low-temperature scale based on resistance of platinum is recognised in the Reichsanstalt's thermometric definitions adopted in 1916 (125), in which the temperature scale below -39° is "defined by the platinum-resistance thermometer which Henning has compared with the hydrogen thermometer." This is the only one of the definitions which is based on a particular existing instrument.

(iv.) *Electrical Resistance of Gold Wire.*—The gold-resistance thermometer has characteristics very much like those of the platinum thermometer. It has, furthermore, certain advantages over platinum for low-temperature work; it is obtainable commercially in much higher purity than platinum, has a resistance-temperature curve which is better adapted to interpolation than platinum, and has a lower inflection point in the resistance curve.

Kamerlingh Onnes and Clay (95) made in 1906 a very exact comparison of the resistance of pure gold wire with that of a standard platinum thermometer, and continued the work in 1907 (96) by studying the effect of

small amounts of impurities on the characteristic constants of the wire.

(v.) *Electrical Resistance of other Metals.*—The electrical resistance of mercury, silver, bismuth, lead, and tin has been measured at various low temperatures determined by gas-thermometers, and wires of these metals have then been used as secondary thermometers.¹

(vi.) *The Thermocouple Constantan : Iron.*—This couple was first compared with the hydrogen thermometer by Holborn and Wien (68), who found from measurements at -78° and -190° that the E.M.F. could be satisfactorily represented by a quadratic formula if the constantan was homogeneous. Inhomogeneous wire varied as much as 2° from the normal. Ladenburg and Krügel (76) in 1899, from measurements at four points with a hydrogen thermometer, found a third-degree equation necessary to represent the results within 1° from 0 to -190° .

The couple was further studied by Kamerlingh Onnes and Crommelin (98) in 1906, who compared it with a constant-volume hydrogen thermometer at various points between -30° and -259° . Down to -217° the E.M.F. could be represented by a four-term formula, which could be established for a new element by calibration at four fixed points. No formula was devised which would represent the entire range accurately.

(vii.) *Other Thermocouples.*—Dewar in 1905 showed that the couple platinum: silver was suitable for measurements of temperature below -250° , where the resistance thermometer becomes relatively insensitive.

The couple gold: silver, though not sensitive at 0° , increases rapidly in sensitiveness at low temperatures, and is better than either constantan: iron or platinum: German-silver (42) below -200° . The gold: silver couple was investigated by Kamerlingh Onnes and Clay (97) in 1908.

§(34) SUMMARY FOR THE RANGE -273° TO 0° .

(i.) *Fixed Points.*—The following fixed points have been determined by measurement with gas-thermometers and form a reliable basis for the establishment and maintenance of the low-temperature centigrade thermodynamic scale:

Melting-point of mercury	$-38.9 \pm 0.05^\circ$
Sublimation point of } carbon dioxide	$-78.5 + 0.016$ ($p = 760$) $\pm 0.05^\circ$
Boiling-point of oxygen	$-183.0 + 0.0126$ ($p = 760$) $\pm 0.05^\circ$
Boiling-point of hydrogen	$-252.7 + 0.005$ ($p = 760$) $\pm 0.05^\circ$

(ii.) *Resistance Thermometers and Thermoelements.*—The platinum-resistance thermometer calibrated at ice, steam, and sulphur points will give temperatures accurate to 0.03° down to -40° . Below that temperature additional calibrations are necessary and

recourse must be had to a standard table of resistance and temperature, with the aid of which it is possible to measure temperature at -200° within 0.05° or less. Gold is preferable to platinum below -200° . Below -250° both are relatively insensitive; managanin or constantan may be used in this region.

Thermo-elements of constantan: iron, platinum: silver, gold: silver, and other combinations, may be used over various parts of the range with the aid of standardised tables. Their sensitiveness varies greatly and the data cannot be briefly summarised.

VII. COMPARISON OF GAS-THERMOMETERS WITH SECONDARY STANDARDS IN THE RANGE 100° TO 500°

§(35) *FIXED TEMPERATURES.*—We shall consider here the fixed temperatures which have been the subject of comparison with gas-thermometers, either directly or through the intermediary of some temperature-indicating device whereby the temperature was directly transferred without reference to the device as an independently operating thermometer.

(i.) *Melting-point of Zinc.*—No melting-points of metals have been determined directly by measurement with a gas-thermometer. The nearest to a direct determination that has been made is Day and Sosman's determination of the melting-point of zinc by what might be called a "substitution" method (35). The temperature of a stirred nitrate bath was first measured near 419° with a constant-volume nitrogen thermometer at initial pressure 500 mm., to the bulb of which three thermocouples were attached. The thermometer bulb was then replaced by a steel vessel of the same shape, containing a charge of zinc in a graphite crucible, with one of the three thermocouples immersed in the metal (this one having been previously at the centre of the bulb in a re-entrant tube). The melting-point thus determined was 419.28° .

An indirect determination, using platinum: platinrhodium thermocouples as intermediaries, was made by Day and Sosman (37) in 1910, in connection with a series from 400° to 1550° , and gave the value 418.2° on the constant-volume nitrogen scale. Subsequent investigations, however, showed that the lack of uniformity in the air-bath designed and used for the high-temperature series caused low readings at 400° , although the difference disappeared above 630° . No weight is attached, therefore, to the first value of 418.2° .

(ii.) *Boiling-points of Naphthalene, Diphenyl, and Benzophenone.*—The only direct determinations of these points are those by Jaquero and Wassmer (73) in 1904, and Crafts (33) in 1913. Jaquero and Wassmer measured the

¹ See article on "Resistance Thermometers."

boiling-points under various pressures by means of a constant-volume hydrogen thermometer with glass bulb, obtaining the following boiling-points under atmospheric pressure :

Naphthalene . . .	217.68° + 0.057 ($p - 760$)
Diphenyl . . .	254.93° + 0.061 ($p - 760$)
Benzophenone . . .	305.44° + 0.063 ($p - 760$)

A later determination on naphthalene by Jaquero and Perrot (72), with a constant-volume hydrogen thermometer with fused silica bulb, gave 217.84° at 760.

Crafts determined the boiling-point of naphthalene directly on the constant-volume nitrogen thermometer at initial pressure 757 mm., obtaining the value 218.06°.

Day and Sosman (35) made an indirect determination of the benzophenone point in 1912, by transfer with thermocouples. The boiling-point on the constant-volume nitrogen scale at initial pressure 500 mm. was found to be 305.87°.

(iv.) *Boiling-point of Sulphur.*—The boiling-point of sulphur has been a rallying-point for all gas-thermometer investigators working in the range 100° to 500°. The determinations before 1890 were not sufficiently accurate to require discussion here. In 1890 Callendar and Griffiths (19) determined the point indirectly, with the platinum-resistance thermometer as intermediary. Chappuis and Harker (24) determined it in the same manner in 1902. Eumorfopoulos (47) made a direct determination in 1908. Another indirect determination with a platinum-resistance intermediary was made by Holborn and Henning (64) in 1911. Finally, direct determinations were made by Day and Sosman (35) in 1912, by Eumorfopoulos (48) in 1914, and by Chappuis (23) in 1917; and an indirect determination by Dickinson and Mueller in 1912 in co-operation with Day and Sosman, using Day and Sosman's nitrogen thermometer (44).

Both constant-pressure and constant-volume thermometers have been used in determining the point. The gases employed and their initial pressures, together with the final results calculated in terms of several scales with the aid of Buckingham's corrections, are shown in Table 9.

The value by Chappuis and Harker was subsequently corrected by the authors themselves in view of new and more accurate determinations of the expansion coefficient of their porcelain bulb. The value by Eumorfopoulos in 1908 was corrected by Callendar and Moss (20) in 1910 with the aid of new determinations of the expansion of mercury, used by Eumorfopoulos to obtain the expansion of his glass bulb. The determinations by Eumorfopoulos in 1914 were made with the constant-pressure nitrogen thermometer at

TABLE 9.—GAS-THERMOMETER DETERMINATIONS OF THE BOILING-POINT OF SULPHUR SINCE 1890

Date.	Author.	Thermometer.	Gas.	Pressure, mm.	Original Figure.	Corrected Figure.	Const. Pr. Nitrogen Scale, $p_0 = 1000$.	Const. Vol. Nitrogen Scale.		Thermodynamic Scale.	Notes.
								$p_0 = 1000$.	$p_0 = 500$.		
1890	Callendar and Griffiths	Const. pr.	Air	760	444.53	..	444.41	444.71	444.81	444.91	Indirect through Pt res. therm.
1902	Chappuis and Harker	Const. vol.	Nitrogen	530	445.2	444.7 *	444.30	444.60	444.70	444.80	
1908	Eumorfopoulos	Const. pr.	Air	760	443.58	444.55	444.43	444.73	444.83	444.93	
1911	Holborn and Henning	Const. vol.	Hydrogen Helium	623 612	444.51 (444.39) †	..	444.01	444.31	444.41	444.51	Indirect through Pt res. therm.
1912	Day and Sosman	Const. vol.	Nitrogen	625	444.45	..	444.05	444.35	444.45	444.55	Direct.
1912	Dickinson and Mueller ‡	Const. vol.	Nitrogen	502	444.28	..	443.88	444.18	444.28	444.38	Indirect through Pt res. therm.
1914	Eumorfopoulos	Const. pr.	Nitrogen	415	444.36	..	444.07	444.37	444.47	444.57	Direct.
1917	Chappuis	Const. vol.	Nitrogen	792	444.13	..	444.03	444.33	444.43	444.53	
			Nitrogen	500.564	444.48	444.49	444.09	444.39	444.49	444.59	

* *Trans. Mem. Bur. Int.*, 1902, xii, 90.

† The value given for "Nitrogen" is calculated from the authors' table of experimental results. They give in their paper only the final mean value on the thermodynamic scale.

‡ Using Day and Sosman's nitrogen thermometer.

two pressures, 792 and 415 mm., and thus permitted a direct calculation of the thermodynamic temperature, which the author places at 444.61°. However, to avoid confusion in the comparisons in the table, we have used a uniform set of corrections for these as well as the other determinations.

It is now fairly certain that the first three determinations in the table are too high. By an unexpected coincidence the original Callendar value on the *constant-pressure air* scale is practically the same as the value on the *thermodynamic* scale now most widely used, but it should be emphasised, in order to avoid possible confusion, that this is a coincidence and not an agreement.

§(36) COMBINATION OF THERMAL PROPERTIES AND FIXED POINTS. (i.) *Electrical Resistance of Platinum Wire*. — The experiments of Callendar (16) in 1886 showed that the platinum-resistance thermometer could be made a very precise and convenient secondary thermometer. He used a constant-volume air thermometer, at an initial pressure of about 1 atmosphere, with soft glass, hard glass, and porcelain bulbs, and determined the resistance of platinum wires, which were sealed into the glass bulbs, at various temperatures from 207° to 624° (671° with porcelain bulb), together with a few check results in a preliminary series at lower temperatures. The results as a whole showed that the resistance could be expressed by the quadratic formula:

$$\frac{R}{R_0} = 1 + \alpha t + \beta t^2,$$

which was put into the form, more convenient for calculation and use, of the two equations:

$$t_{pt} = 100 \times \frac{R - R_0}{R_{100} - R_0}$$

$$\text{and } t - t_{pt} = \delta \left[\left(\frac{t}{100} \right)^2 - \frac{t}{100} \right].$$

The comparison made in 1891 by Callendar and Griffiths (19) has been referred to in §(29) ii. Except in three cases the agreement with the constant pressure air thermometer was within 0.012°.

A further exact test of the platinum-resistance formula was made by Chappuis and Harker (24) in 1902. Having found that the pressure of hydrogen in a glass bulb decreased progressively at 180° and higher, the authors abandoned hydrogen and used nitrogen at initial pressures of 392 to 793 mm. One series was also made with a porcelain bulb. Three resistance thermometers were used. As a result of comparisons at a large number of points, it appeared that the Callendar formula would represent the true temperature within 0.1° between 100° and 250°, and within 0.3° between 250° and 450°. The authors con-

servatively stated that "rigorous conclusions cannot be drawn concerning the application of the Callendar method to the calibration of platinum thermometers. Further comparisons are needed with the gas thermometer and of various resistance thermometers with each other."

The desired recomparison was not completely forthcoming until 1911, when Holborn and Henning (64) published their work on nitrogen, hydrogen, and helium thermometers from 200° to 450°, although comparisons at 150° and 200° were published by these authors (63) in 1908.

The 1908 comparisons showed that, when the sulphur point was taken as 445.0°, temperatures near 150° and 200°, interpolated by the resistance thermometer, agreed with the centigrade thermodynamic scale within 0.05°. Recalculation on the basis of 444.55° for the sulphur point, however, makes the deviations 0.04° to 0.07° larger, but still leaves the average agreement within 0.1°.

In the 1911 comparisons differences of 0.05° to 0.11° were found between bulbs of Jena glass and fused silica containing nitrogen, but these differences were ascribed to uncertainty in the expansion of the Jena glass. The nitrogen-in-silica temperatures differed from those with helium and hydrogen by about the amount to be expected from Berthelot's and Buckingham's gas-thermometer corrections. Taking the temperatures obtained with hydrogen and helium in glass and silica as standard, therefore, it appeared that these temperatures could be interpolated with an accuracy within 0.03° at 200° and 0.05° at 400° with the aid of the Callendar formula and calibration at ice, steam, and sulphur points.

(ii.) *Platinum-metal Thermocouples*. — Holborn and Day (61) made in 1899 the first thorough-going comparison of the platinum: 90 platinum, 10 rhodium couple with a gas-thermometer. They continued the work in 1900, revising the earlier data with the aid of new values for the expansion of the bulbs. Their comparisons with the constant-volume nitrogen thermometer extended from 195° up. It was found possible to represent the E.M.F. in terms of temperature by an equation of the form

$$e = -a + bt + ct^2$$

over the range 250° to 1100°, with an accuracy of 1° or better. A similar formula held for couples of platinum: 90 platinum, 10 ruthenium and platinum: rhodium over the same range. The couple platinum: iridium, however, deviated from this formula below 400° by several degrees.

The nitrogen-thermometer comparisons by Day, Clement, and Sosman (36) (1908–1912) showed that a quadratic equation would repre-

sent the E.M.F. of the platinum : platinum-rhodium couple from 300° to 1100° within 0.3° .

(iii.) *Copper-constantan Thermocouple*.—Although this couple has not been directly compared with a gas-thermometer at a series of temperatures between 100° and 500° , Adams and Johnston (3) were able, by utilising the measurements of Day and Sosman in 1912 at 300° , and by measuring the E.M.F. at fixed points which had been otherwise interpolated, to show that the couple will reproduce temperatures between 100° and 360° with an accuracy of 0.02° .

(iv.) *Interpolated Fixed Points*.—Day and Sosman determined the melting-point of cadmium by interpolation with thermocouples calibrated against the nitrogen thermometer.

Holborn and Day, after calibrating platinum : platinum-rhodium thermocouples against the nitrogen thermometer and obtaining their law of variation, used these couples as secondary thermometers to determine the melting-points of cadmium, lead, and zinc.

Holborn and Henning, after satisfying themselves that their resistance thermometers, with the Callendar formula, gave constant-volume hydrogen and helium temperatures with an accuracy of 0.03° to 0.05° , interpolated the melting-points of tin, cadmium, and zinc, and the boiling-points of naphthalene and benzophenone, with their resistance thermometers.

Crafts (32) determined the boiling-points of naphthalene and benzophenone by means of mercury thermometers standardised against a constant-volume hydrogen thermometer, obtaining the values 218.08° and 306.1° respectively.

In addition to the foregoing data, which may be called "primary" interpolations, there have been various "secondary" interpolations of fixed points not directly connected with any gas-thermometer observations, but based solely upon other fixed points which had been determined by means of gas-thermometers, taken in conjunction with a law of variation made probable by still other gas-thermometer observations. Such interpolations, including those by Heycock and Neville (57), Callendar and Griffiths (19), Waidner and Burgess (122), Travers and Gwyer (113), and Adams and Johnston (3), are, strictly speaking, outside the scope of this article, but are included here for the sake of comparison. All of the interpolated data, together with the direct and indirect gas-thermometer determinations, are collected in Table 10.

§ (37) THERMAL PROPERTIES. (i.) *Index of Refraction of Gases*.—In 1895 D. Berthelot (10) suggested that the density of a gas at a known pressure (atmospheric), and hence its temperature, could be determined by measuring its

index of refraction. Tests of the method at the boiling-points of alcohol (78°), water, and aniline (184°) gave deviations of 0.05° to 0.12° at 78° , 0.03° to 0.12° at 100° , and 0.08° to 0.33° at 184° , from the known boiling-points of these substances on the normal hydrogen scale. The method was therefore considered promising enough to be extended to temperatures above 500° . A fuller discussion of it will be found in Part VIII. of this article. From the results given above it appears that in the range just above 100° the method is not as precise as mercurial or resistance thermometry.

(ii.) *Total Radiation of a Black Body*.—Valentiner (115) has obtained values of σ , the constant of the Stefan-Boltzmann law, from measurements at the boiling-points of water and of sulphur. These are fully discussed elsewhere.¹

§ (38) SUMMARY FOR THE RANGE 100° - 500° .

(i.) *Resistance Thermometry*.—The Callendar formula applied to a platinum-resistance thermometer meeting the specifications of the Reichsanstalt,² calibrated at ice, steam, and sulphur points, will give either normal hydrogen scale temperatures or centigrade thermodynamic temperatures, depending upon the scale in which the sulphur point is taken, within 0.05° at 200° and within 0.1° at 400° .

(ii.) *Thermocouples*.—A cubic formula for e in terms of t , applied to the copper-constantan couple calibrated at three fixed points such as the boiling-points of water, naphthalene, and benzophenone, will give normal hydrogen or thermodynamic scale temperatures within 0.05° in the range 100° to 350° . A platinum : platinum-rhodium couple calibrated at two points to determine its deviation curve will, when used with Adams' table (1), give temperatures within 0.2° at 200° and 0.3° at 500° .

(iii.) *Fixed Points*.—The following fixed points are suitable for the establishment and maintenance of a temperature scale with the aid of secondary thermometers, and are known on the thermodynamic scale with the accuracy indicated, assuming the materials to be the purest now obtainable :

Boiling-point of naphthalene	$217.95 + 0.058(p - 760)$	$\pm 0.05^{\circ}$
Melting-point of tin	$231.85 \pm 0.1^{\circ}$	
Boiling-point of benzophenone	$305.9 + 0.063(p - 760)$	$\pm 0.1^{\circ}$
Melting-point of cadmium	$320.9 \pm 0.1^{\circ}$	
Melting-point of zinc	$419.4 \pm 0.2^{\circ}$	
Boiling-point of sulphur	$444.55 + 0.0908(p - 760)$ $- 0.000047(p - 760)^2 \pm 0.1^{\circ}$	

Some of these substances are now obtainable as certified samples from the national standardising bureaux (for example, tin and zinc from the National Bureau of Standards of the United States).

¹ See article on "Radiation, Determination of Constants," Vol. IV.; also Part VIII. of the present article.

² See summary of Part V. of this article.

TABLE 10
INTERPOLATED VALUES OF FIXED POINTS IN THE RANGE 100°-500° COMPARED WITH GAS-THERMOMETER DETERMINATIONS
(ALL ON THERMODYNAMIC SCALE)

Author.	Date.	B.P. Naphthalene.	M.P. Tin.	B.P. Benzophenone.	M.P. Cadmium.	M.P. Lead.	M.P. Zinc.	Basis.
<i>Direct or Indirect Gas-thermometer Determinations.</i>								
Jaquero and Wassmer .	1904	217.68	..	305.44	* Constant-volume hydrogen.
Jaquero and Perrot .	1905	217.84	
Day and Sosman .	1912	305.91	419.4	Constant-volume nitrogen.
Crafts	1913	218.08	
<i>Primary Interpolations.</i>								
Crafts	1883	218.08	..	306.1	{ Mercury thermometers standardised by constant-volume hydrogen thermo- meter.
Holborn and Day . .	1900	321.7	326.9	419.0	
Holborn and Henning .	1911	217.96	231.83	305.89	320.92	..	419.40	{ Pt. res. thermometer and helium thermometer.
Day and Sosman . .	1912	320.9	{ Pt.:PtRh couple and nitrogen thermo- meter.
<i>Secondary Interpolations.</i>								
Griffiths	1891	218.04	{ Pt res. thermometer standardised at 0, 100, and 444.55.
Callendar and Griffiths .	1891	217.94	231.7	305.82	320.7	327.7	417.6	
Heycock and Neville .	1895	..	231.9	419.0	
Travers and Gwyer .	1905	218.04	..	305.80	
Waidner and Burgess } (123), (122)	1910	217.95	231.88	305.95	320.92	327.33	419.23	{ Copper - constantan thermoelements between 217.95, 305.9, and 419.4.
Adams and Johnston .	1911	..	231.73	..	320.92	327.39	..	

VIII. COMPARISON OF GAS-THERMOMETERS WITH SECONDARY STANDARDS IN THE RANGE 500° TO 1600°

§ (39) HISTORY. (i.) *Prinsep*, 1828.—The first high-temperature thermometer based on the expansion of gases, so far as we now know, was made by Prinsep (102) and described by him in 1828. He used a bulb of gold, connected with a sensitive manometer with which to maintain the gas (air) at constant pressure within, and connected also with a reservoir of olive oil; the expansion of the air in the bulb displaced a proportionate amount of oil, which was caught and weighed. With this apparatus Prinsep made excellent temperature measurements, chiefly of the melting-points of the alloys of gold, silver, and platinum, which bear his name, and are still sometimes used.

(ii.) *Pouillet*, 1836.—Prinsep was quickly followed by Sir Humphry Davy and several others, all employing the expansion of air at constant pressure, but none contributing materially to the improvement of Prinsep's apparatus until Pouillet (101) constructed his instrument in 1836. Pouillet's bulb was of platinum, which enabled him to reach the highest temperatures, and his experimental procedure, with but slight modifications, is that employed in later years by Callendar and his associates. It was Pouillet also who made and calibrated the first practical thermo-element (platinum-iron), who anticipated the method of measuring temperature through determinations of the specific heat of platinum subsequently developed by Violle, and who made some study of the radiant energy sent out by glowing solids. In varying degree, and with many of the inevitable limitations of the pioneer, Pouillet not only established gas-thermometry upon a sound basis, but introduced several of the important practical methods of pyrometry which have been in use since his time.

Following Pouillet, therefore, the advancement of pyrometric measurement became to a considerable degree a question of perfection of experimental detail rather than of the development of new principles, and so, with one or two exceptions which will be noted presently, it has since remained. Regnault in particular made in 1847 a number of improvements in the Pouillet instrument (103).

The first gas-thermometer which measured the expansion of the gas under constant-volume appears to have been built by Silbermann and Jacquelin in 1853, but it was only indifferently successful. Effective use was first made of the method in the work of Becquerel, described below.

(iii.) *St. Claire-Deville and Troost* (39), 1857.—It was soon after this that a real catastrophe

occurred in the development of the gas-thermometer. Deville and Troost (1857), desiring to use a heavier gas in place of air, introduced iodine into a bulb of porcelain and made determinations of a number of constant temperatures, most conspicuous among which, in the discussion which followed, was the boiling-point of zinc, which they ascertained to be 1040°.

(iv.) *Edmond Becquerel* (9), 1863.—Becquerel followed in 1863, using the Pouillet apparatus with platinum bulb and air as the expanding gas, and reached the conclusion that zinc boiled at 932°, more than 100° lower. In the controversy which followed, and which was maintained from both sides with considerable bitterness, these observations were repeated by both observers with substantial confirmation of the first results, Deville and Troost maintaining from experiments of their own that Becquerel's platinum bulb was permeable to hot gases, and that his results must of necessity be too low. To this contention Becquerel replied convincingly by using a porcelain bulb himself (still retaining air as the expanding gas), with both the constant-volume and constant-pressure methods of measurement, and announced a result (891°) even lower than his previous determination. Notwithstanding this, Deville and Troost were unwilling to regard the result as conclusive, and looked upon the discrepancy between Becquerel's earlier and later results (932° and 891°) with unconcealed suspicion. They reiterated their belief that the platinum bulb was permeable and that Becquerel's results with porcelain bulbs were still too low through failure to expose the bulb directly to the zinc vapour. Becquerel's bulb had been shielded from the direct action of the zinc by a protecting tube. Deville and Troost then repeated their own measurements and again obtained their earlier result. Becquerel, following, insisted that his measurements with the platinum bulb were not seriously affected by permeability to hot gases, a property with which he appeared to be familiar, and explicitly criticised the use of iodine by Deville and Troost.

The discussion ended here for the moment without a decisive issue, but subsequent experience has substantially confirmed Becquerel in his contention and his numerical results. The high value obtained by Deville and Troost was undoubtedly due chiefly to the dissociation of the iodine at high temperatures.

The real catastrophe in the development of the gas-thermometer, however, does not lie in the uncertainty of the results obtained with it by these distinguished observers, nor yet in the subsequent discovery that iodine is an inappropriate expanding medium with which to measure temperature; but rather

in the discredit in which the platinum bulb came to be held and the universal substitution therefor of porcelain—a material of wholly uncertain chemical composition and physical characteristics. This was a backward step which was not retrieved for more than thirty years.

Deville and Troost (40) then entered upon a long series of experiments with porcelain glazed inside and outside with feldspar, in the course of which it appeared that the expansion of the bulb, a factor of great importance both then and now in gas-thermometry, was variable with the temperatures to which it had previously been exposed. These irregularities diminished with continued use, and were thought to become negligible in bulbs of Bayeux porcelain after a few heatings to a very high temperature.

(v.) *Regnault* (104), 1861.—During the progress of the above investigation Regnault was at work upon a displacement method (boiling mercury in an iron flask and estimating the temperature from the quantity remaining in the flask after cooling), which did not prove satisfactory. Schinz, Berthelot, and Weinhold suggested some modifications of this and other contemporary methods, but none of them proved of permanent value.

(vi.) *Erhard and Schertel* (45), 1879.—Erhard and Schertel redetermined the melting temperatures of the Prinsep alloys in 1879, using a bulb of Meissen porcelain and air as expanding gas with considerable success. Their work contributed little of novelty, but was carefully done, and the results have since been extensively used.

In 1880 Deville and Troost reappeared in the field, after a long silence, and also proposed a displacement scheme containing some improvements over the apparatus proposed by Regnault. Nitrogen was here used in place of air, but otherwise the method possessed insufficient accuracy to secure for it general approval. In the same year they published a summary of all their work on boiling zinc, giving 942° as the mean of 27 determinations, which was (for that time) in good agreement with Becquerel's first value, 932° .

(vii.) *Violle* (120), 1882.—In the same year (1882) *Violle*, using Deville and Troost's methods and apparatus, found zinc to boil at 930° , and thus added a further degree of probability to the determination of Becquerel. *Violle* continued his researches by determining with the gas-thermometer the specific heat of platinum for a number of temperatures up to 1200° .

In the decade between 1882 and 1892 contributions to gas-thermometry and the measurement of high temperatures are few and unimportant, but investigations were

begun in those years on both sides of the Atlantic, namely, those of Barus at the U.S. Geological Survey in Washington and of Holborn and his colleagues at the Reichsanstalt in Charlottenburg.

(viii.) *Barus* (5, 7), 1889, recognised, as no observer who preceded him had done, the superlative importance of a uniform temperature distribution about the gas-thermometer bulb for purposes of high-temperature measurement. He sought to avoid irregularities due to the shape of the apparatus and the use of gas flames by a method of great ingenuity, but also of great technical difficulty. He enclosed his bulb within a rapidly revolving muffle (5, 6), which by its motion protected every portion of the bulb from direct exposure to a particularly hot or a particularly cold portion of the adjacent furnace. This complicated furnace structure and consequently inaccessible position of the bulb made it necessary to use thermo-elements which were first calibrated by exposure in the furnace with the bulb and then used independently to measure other desired temperatures. The thermo-element has continued in general use in this intermediary rôle since that time.

(ix.) *Holborn and Wien*, 1892.—In the same year in which Barus published his final memoir on the gas-thermometer and the thermo-element (1892), Holborn and Wien published a paper (66) covering nearly the same ground in the same general way, but with somewhat different results. Both used air as the expanding gas, both used thermo-elements to transfer the standard gas temperatures over to the substance to be measured; but Holborn and Wien attained to higher temperatures (above 1300°), while Barus took much greater precautions than his German contemporaries to secure a uniform temperature about his bulb. The arrangement adopted by Holborn and Wien possessed the further advantage that the thermo-element was entirely enclosed within the bulb itself and so was well protected against the contaminating influence of furnace gases, besides giving a truer record of the actual temperature of the expanding gas. Over against this it should be stated that the volume of the unheated portions of their bulb and manometer connections, which then constituted the chief source of error in all gas-thermometer measurements, was dangerously large.

After 1892 Barus turned his attention to other things, but Holborn and Wien published a second article (67) in 1895 confirming and extending their earlier results. By employing a specially refractory porcelain bulb they were able to continue the gas measurements nearly to the melting-point of nickel.

(x.) *Holborn and Day* (61), 1899.—With the advancing demands of science for trust-

worthy high-temperature measurements, the existing differences in the absolute temperature of the melting-point of gold, which is an ideal substance for a temperature constant, soon came to be regarded as unsatisfactory, and the whole problem was again taken up at the Reichsanstalt by Holborn and Day, with a view to clearing up these differences. At that time the gas-thermometer was in serious danger of falling into disrepute as a physical instrument of precision. Holborn and Day began by using bulbs of Royal Berlin porcelain, but, after the investigation had proceeded for a year or more, abandoned them definitely and permanently to return to the old platinum bulb of Pouillet, with an appropriate gas (nitrogen) which could not penetrate the bulb wall. A further improvement of inestimable value in attaining constant and reproducible conditions was made when electric heating-coils were substituted for gas. With this change the contamination of the thermo-elements through the action of combustion gases, the danger of one or other of these gases penetrating the bulb wall itself, irregularities of temperature about the bulb, and inadequate control of the heat supply, were all eliminated or much reduced in magnitude at a single stroke. Several metal melting-points were established as points of reference for the high-temperature scale, which soon found general acceptance and were almost universally used until within a few years.

Since the beginning of the present century, but four attempts have been made to reach 1000°C . with the gas-thermometer. These may be taken up in the order of their publication as follows: (1) J. A. Harker (1904), using a porcelain bulb and nitrogen; (2) Jaquero and Perrot (1905), using a bulb of "quartz glass" and various gases; (3) Holborn and Valentiner (1906), using one bulb of platinum containing 20 per cent of iridium and one of pure iridium, both with nitrogen as the expanding gas; and finally (4) Day and Clement (1908), and Day and Sosman (1910), using bulbs of platinum containing 10 per cent of iridium and 20 per cent of rhodium respectively.

(xi.) *Harker* (51).—The work of J. A. Harker at the National Physical Laboratory (England) does not differ in any important particular from the work of Holborn and Day which immediately preceded it at the Reichsanstalt. His instrument was an exact duplicate of the Reichsanstalt instrument by the same maker, except that the bulb was of porcelain instead of platinum-iridium.

(xii.) *Jaquero and Perrot* (72), 1905.—Jaquero and Perrot sought to establish a high-temperature scale from which two of the important sources of uncertainty in previous work should be eliminated: (1) the uncer-

tainty due to differences in the expansion of the various available gases; (2) any uncertainty which might enter the problem through the expansion of the containing vessel (bulb). Their results toward the accomplishment of their first object have been discussed in Part III. To accomplish the second they selected for the material of their bulb a substance whose expansion coefficient was less than one-tenth as great as any which had been employed for the purpose up to that time. Both improvements afforded most valuable information.

(xiii.) *Holborn and Valentiner* (65), 1906.—The experiments of Holborn and Valentiner contemplated another definite and important step in advance. Theirs was the first serious effort to extend the gas scale itself from 1150°C ., where all previous investigations had been halted, to 1600°C . The difficulties confronting such an undertaking are obvious and of an insistent kind. Of the limited number of substances available for use as bulbs none is without serious limitations at these extremely high temperatures. Porcelain becomes soft and its walls both absorb and generate gas in prohibitive quantities; silica glass devitrifies; pure platinum is very soft and is permeable to hydrogen; when stiffened with iridium or rhodium it is the best material available but the iridium is destructive to the thermo-elements, and the bulb is likely to develop leaks and is permeable always to hydrogen if but a trace of the gas or of water-vapour is about. Furthermore, the difficulty of maintaining a constant temperature about a bulb of 200 c.c. capacity increases at these temperatures, and the difficulty of measuring with thermo-elements within the furnace is greatly increased by the conductivity of all insulating material. It is also a matter of no inconsiderable difficulty to generate and to regulate accurately the quantity of heat required for a bulb of this size under conditions where all electrical insulation begins to break down, and to protect the mercury manometer from so hot a furnace without removing it to an impracticable distance.

Their effort demonstrated beyond peradventure that the extension of the gas scale to 1600° was practicable.

(xiv.) *Day, Clement, and Sosman* (1908-1912).—Having in mind the diminution of errors due to lack of uniformity of temperature in an air-bath, Day and Clement (34) in 1908 constructed a gas-thermometer with a platinum-wire-wound furnace especially designed to produce uniformity, and with a bulb made of an alloy of 90 parts platinum and 10 parts iridium. They also prevented both variable and constant errors caused by the difference in pressure between the inside and outside of the bulb, by enclosing it in a furnace

jacket containing nitrogen or air at the same pressure as that within the bulb. They further reduced the magnitude of the constant correction due to the "unheated space" to a much smaller value than had been attained before. By means of a cap having the shape of the mercury meniscus, the unheated space ratio was reduced to 0.0015.

To avoid the errors due to contamination of the intermediary thermocouple by iridium volatilising out of the bulb, this gas-thermometer was then further improved by the substitution of a bulb made of an alloy of 80 parts platinum and 20 rhodium in place of the platinum-iridium bulb. With this apparatus Day, Sosman, and Allen (37, 38, 36) made in 1908-1910 an extended series of gas-thermometer observations, using nitrogen at initial pressures of 217-347 mm., and platinum-platinrhodium thermocouples to transfer the temperatures to a series of melting-points of metals and silicates as fixed temperatures. All of the materials used were analysed to determine their purity.

§ (40) FIXED TEMPERATURES. (i.) *Melting-points of Metals.*—Several of the earlier investigations of the high-temperature scale made comparisons between the gas-thermometer and the melting-points of metals.

E.M.F., and radiation, and the fixed temperatures determined in connection therewith were, so to speak, tertiary standards. A discussion of these measurements belongs properly in the third part of this section.

The only exception was the series of measurements of the melting-point of gold by Jaquero and Perrot (72) in 1905. They determined the temperature of the melting metal directly in terms of constant-volume thermometers containing air, nitrogen, oxygen, carbon monoxide, and carbon dioxide, obtaining as a mean value for the melting-point $1067.4 \pm 1.8^\circ$.

The most accurate determinations of metal melting-points above 500° in terms of a gas-thermometer are those of Day, Sosman, and Allen (37) in 1910. They first measured the E.M.F. of several platinum-platinrhodium couples at a fixed temperature, then placed these couples together with the thermometer bulb in an electric resistance furnace and brought the temperature as nearly as possible to the same point. The determinations are thus nearly independent of the law of variation of the thermocouples with temperature.

Their melting-points, in the scale of the constant-volume nitrogen thermometer at initial pressure 350 mm., are given in Table 11.

TABLE 11
MELTING-POINTS OF METALS AS DETERMINED BY DAY, SOSMAN, AND ALLEN

Metal.	Point.	Atmosphere.	Crucible.	Total Impurities in Metal, per cent.	Temperature.
Antimony	{ Melting and freezing }	Carbon monoxide	Graphite	0.031	629.85 ± 0.3
Silver .	"	"	"	0.003	960.0 ± 0.7
Gold . .	"	"	"	< 0.005	1062.4 ± 0.8
Copper .	"	"	"	0.008	1082.6 ± 0.8
Nickel .	"	{ Hydrogen and nitrogen }	Magnesia and magnesium aluminate }	0.165	1452.3 ± 2.0
Cobalt .	"	"	Magnesia	0.049	1489.8 ± 2.0
Palladium	"	Air	Pure magnesia	0.025	1549.2 ± 2.0

Erhard and Schertel's measurements in 1879 on gold and silver were direct comparisons, made by placing the melting metal and the air-thermometer bulb side by side in the furnace. Becquerel's determination of the silver point in 1863 was an indirect comparison, using a platinum-ruthenium thermocouple as intermediary. These earlier measurements were admittedly of the order of accuracy of $\pm 5^\circ$, and therefore need not be considered in comparison with the more exact measurements made since 1890.

Between 1890 and 1910 most of the high-temperature gas-thermometer observations were directed toward determining the law of variation of secondary thermometric properties, such as electrical resistance, thermal

(ii.) *Boiling-points of Metals.*—Barus, in beginning his work in 1882, realised the importance of securing uniformity of temperature about the gas-thermometer bulb, and was impressed by the advantages of employing vapours of boiling liquids for this purpose. He accordingly devoted considerable time to the study of vapour baths containing boiling mercury, sulphur, cadmium, zinc, and bismuth.

Of the higher-boiling metals only zinc has been studied directly with a gas-thermometer. Holborn and Day in 1899 made measurements with one of their porcelain bulbs immersed in the vapour of boiling zinc, and obtained 916° - 920° as the boiling-point.

The difficulties of handling an apparatus

containing a considerable volume of boiling metal led to its abandonment for work above 500°, and no high-temperature metal boiling-points have been determined with the gas-thermometer since 1899, either directly or with a transfer device.

(iii.) *Melting-points of Inorganic Compounds.*—The work of Day, Clement, Sosman, and Allen at the Geophysical Laboratory was inspired by the need of a more exact thermometric scale above 1100° for use in investigations on the silicates, and several silicates were accordingly used as fixed temperatures of reference. These are contained in Table 12, together with the melting-points of two salts determined by White with thermocouples intercompared with the gas-thermometer couples.

TABLE 12
MELTING-POINTS OF INORGANIC COMPOUNDS
AS DETERMINED BY DAY AND SOSMAN

Compound.	Formula.	Temperature.
Sodium chloride .	NaCl	800 ± 1
Sodium sulphate .	Na ₂ SO ₄	884 ± 1
Lithium metasilicate	Li ₂ SiO ₃	1201 ± 1
Diopside . . .	CaMgSi ₂ O ₆	1391 ± 1.5
Anorthite . . .	CaAl ₂ Si ₂ O ₈	1550 ± 2

§ (41) THERMAL PROPERTIES.—The following reproducible thermal properties have been studied with the aid of gas-thermometers in the range above 500° C.:

The specific heat of platinum; the index of refraction of air; the total radiation from a black body; the radiated energy corresponding to a given wave-length in the radiation from a black body.

(i.) *Specific Heat of Platinum.*—The dependence upon temperature of the mean specific heat of platinum from 0° was found by Violle (117) with the aid of Deville's constant-volume air-thermometer with porcelain bulb, to be given by the equation

$$C = 0.0317 + 6 \times 10^{-6}t$$

from 100° to 1177°. The specific heat of platinum was then used by Violle as a secondary thermometric property for the determination of the melting-points of silver, gold, and copper (119); also, by extrapolation, for the melting-points of palladium (118), platinum (117), and iridium. The values are now only of historical interest.

The measurement of heat energy is logically one of the simplest of physical measurements. Practically, it is one of the most difficult, so elusive and unconfined is the thing which it is desired to measure. For this reason, and also because of difficulties in the manipulation, thermometry by calorimetric methods has never become popular.

(ii.) *Index of Refraction of Air.*—Experiments at pressures of 1 to 19 atmospheres and at temperatures of 0° to 80° C. had shown that within the limits of error of the measurements the refraction $n-1$ of air and of cyanogen gas was proportional to the specific volume of the gas whether the change in specific volume was produced by pressure or by heat. The measurement of refractive index thus offered a means of realising a secondary constant-pressure gas-thermometer.

D. Berthelot in 1898 utilised this fact in a "gas-thermometer" (10, 11), with which he measured the melting-points of silver and gold by direct comparison (12).

Strictly speaking, the method is not only secondary, but as used by Berthelot constituted a wide extrapolation of a law established experimentally only at low temperatures. Investigations made since the date of Berthelot's experiments indicate that gases follow the Lorenz-Lorentz formula for the relation of refractive index to density at constant temperature; when the temperature is changed, an effect independent of the diminution in density with rising temperature is indicated, but its amount and magnitude are by no means certain.¹

The results obtained by Berthelot seem to have had a precision of about $\pm 1.5^\circ$ at 1060°. The "end corrections" of the furnace tube constitute the most serious source of error. The method has not been further used since the time of his experiments.

(iii.) *Total Radiation of a Black Body.*—E, the total energy radiated by a black body per second per unit of surface, and θ , the absolute temperature, are related according to the Stefan-Boltzmann law:

$$E = \sigma \theta^4,$$

in which σ is a constant.

Although originally discovered by Stefan as an empirical relation, this law is from one point of view not in need of confirmation by comparison with a gas-thermometer, for Boltzmann subsequently showed that this relation between temperature and radiated energy depends only upon the principles of thermodynamics and the electromagnetic theory. If these be taken as fundamental, the Stefan-Boltzmann law might therefore itself be used as an independent definition of θ .

For this purpose it is necessary only to go back to Part I. and, starting with the definition of the absolute thermodynamic scale and the arbitrary numerical difference of 100° between melting ice and boiling water, to make measurements of radiation at those temperatures. The scale is then completely determined.

¹ See discussion in Loria, *Die Lichtbrechung in Gasen*, pp. 29-39 (Braunschweig, 1914).

The experimental precision attainable in radiation measurements at 0° and 100° is, however, too low to permit of a successful independent definition of a temperature scale by this means. It is necessary, in order to obtain an accurate value for σ or an accurate ratio of θ 's, to make absolute energy measurements at higher temperatures, or relative energy measurements at temperatures widely separated, such as 1500° and 1000° . The total radiation scale thereupon becomes, in effect, a secondary scale, dependent upon the gas-thermometer for the definition of its basic temperatures.

But the radiation scale is not dependent upon the gas-thermometer to the extent that the platinum-resistance thermometer is dependent. It has a sufficiently sound and well-established theoretical basis to have attained a practically independent status. If the gas-thermometer ventures too far into the high-temperature region where it is losing its precision, but where the total radiation thermometer is gaining precision or at least holding its own, the gas-thermometer will reach a point where it can no longer compete with its rival. Part of the present disagreement over the temperature scale above 1200° can be reduced to this simple question: Is the gas-thermometer or the radiation thermometer ahead in this race at the 1500° level? It is generally admitted that the gas-thermometer scale has no competitors at 1000° and the radiation-thermometer scale none at 2000° . In the intervening range the favour of the experimental physicist will turn toward the scale which possesses the greater experimental precision.

In answer to this question, an examination of the experimental data shows that the gas-thermometer still has the advantage at 1500° . Its indications certainly are capable of an accuracy at that temperature of better than 2° . To obtain this accuracy on the radiation scale calls for measurements equivalent to the determination of σ to within 0.45 per cent, or to within 0.026×10^{-12} , taking the value of σ as 5.70×10^{-12} . The value of σ or the measurements of intensity-ratios are hardly yet certain to that degree of accuracy.

As for the constant itself, no direct determination of σ at high temperatures with direct reference to a gas-thermometer has ever been made. Valentiner's determinations (115) are perhaps the most closely related to gas-thermometer temperatures, being in terms of platinum-platinrhodium thermocouples standardised by comparison with Holborn and Valentiner's constant-volume nitrogen thermometer up to 1600° . Valentiner's first result was admittedly inaccurate by 4 per cent (116), and Coblentz believes that "a conservative estimate of the total correction

to Valentiner's original data is 5 to 6 per cent."

A discussion of the twelve or more other determinations of σ need hardly be undertaken here, as the subject is more fully considered in the article on Radiation Laws. Reference need only be made to Coblentz's detailed summary (30) of the status of the constant. The original determinations of $10^{12}\sigma$ quoted by Coblentz range from 5.30 to 6.51. These data he has recalculated, using corrections obtained from his own extensive experiments (26, 29), thereby reducing the range to 5.48-5.9, leaving several uncertain. The mean, 5.7, of so motley a collection would have very little authority did it not happily coincide with the much more accurate value, 5.722 ± 0.012 , determined by Coblentz¹ (31); this is, again, in excellent agreement with several fundamental physical constants, as shown by Millikan (84).

(iv.) *The Energy corresponding to a given Wave-length in the Radiation from a Black Body.*—From the Wien-Planck law, as revised by Planck (100), for the distribution of energy in the spectrum of a black body, it follows that if E_1 represents the energy intensity, corresponding to the wave-length λ , radiated from a black body at absolute temperature θ_1 , and E_2 the corresponding energy for the same wave-length, but at temperature θ_2 , then

$$\frac{E_1}{E_2} = \frac{e^{C_2/\lambda\theta_2} - 1}{e^{C_2/\lambda\theta_1} - 1}.$$

For values of λ in the visible portion of the spectrum and temperatures attainable in the laboratory, the effect of neglecting the term -1 is less than 1 per cent in the ratio, corresponding to less than 1° at 1500° ; this simplification is therefore usually made, and the relation put into the form

$$\frac{1}{\theta_2} - \frac{1}{\theta_1} = \frac{\lambda}{C_2} \log_e \frac{E_1}{E_2},$$

which is the usual equation for the optical pyrometer.

To what extent is the Planck radiation law a direct deduction from the Stefan-Boltzmann radiation law? Both Wien and Planck derived their original law from purely theoretical grounds, but experimental results at long wave-lengths showed that the "constant" C_2 in the original form was not a constant (78). Planck then revised the derivation, again on a purely theoretical basis, but not without assumptions which may or may not be true. The conservative view that should be taken in defining a temperature scale must therefore consider the Planck radiation law to be strictly experimental, valid over the range

¹ See article "Radiation, Determination of the Constants," Table I. and § (10), Vol. IV.

and to the degree of accuracy for which it has been experimentally proved.

From this standpoint any temperature scale based on the law is a purely secondary scale, no more accurate and entitled to no greater validity than the gas-thermometer temperatures upon which the value of the constant C_2 is based. It is evident, furthermore, that when they are viewed as secondary scales the optical scale (with constant C_2) is logically in a much less favourable position than the total radiation scale (with constant σ), since ratios of total radiation can be determined with a temperature range of say 100° to 1200° , whereas the corresponding range for C_2 must begin within the region of visible radiation due to temperature, or at about 700° , and must be further handicapped by the rapid fall in sensitivity of the optical measurement when the temperature is lowered from 1200° to 700° .

There has been no determination of C_2 accompanied by direct measurement of the temperature by a gas-thermometer, but several determinations have been closely related to gas-thermometer temperatures by the transfer of temperature with thermocouples.

The first of these was by Lummer and Pringsheim in 1900 at the Reichsanstalt (79), using temperatures transferred by platinum-platinrhodium couples from Holborn and Day's nitrogen thermometer. They obtained values of C_2 for different wave-lengths, from measurements at 790° to 1430° C., varying from 1.450 to 1.469, with a mean of 1.458.

Holborn and Valentiner (65) in 1907 likewise transferred their temperatures thermoelectrically from their nitrogen thermometer to the black body. Their temperatures ranged from 1100° to 1685° , and the values of C_2 obtained ranged from about 1.38 to about 1.46; mean, 1.420 ± 0.014 .

Another step removed from the gas-thermometer are those determinations based upon fixed temperatures, such as melting-points, which have been previously determined by a gas-thermometer.

Nernst and von Wartenberg's photometric measurements (85) in 1906, at wave-length 0.590μ and at the melting-points of gold and palladium (1063° and 1550° C., respectively, by the nitrogen thermometer), correspond to a value of 1.438 for C_2 .

Hoffmann and Meissner (58, 59) in 1912 and 1913 made spectrophotometric observations in various wave-lengths of light at the melting-points of gold and palladium. On the same temperature basis as above, their data correspond to values of C_2 from 1.440 to 1.447.

Hyde, Cady, and Forsythe (70, 71), likewise, have measured with a Holborn-Kurlbaum

pyrometer the ratio of intensities at the gold and palladium points, at an effective wave-length of 0.666μ . The result corresponds to $C_2 = 1.447$.

Similar measurements by Mendenhall (83) correspond to a value of 1.439. Another series, based upon the gas-thermometer temperature of 1330° C., and a second temperature 2460° C. based upon total radiation, also gave the value 1.439.

Mendenhall's second series is a step further removed from direct dependence on the gas-thermometer, being based on only one fixed temperature. The same is true of the series of measurements by Warburg, Leithaeuser, Hupka, and Mueller (126) at the Reichsanstalt in 1913. Their basic point was the gold melting-point, but higher temperatures (1400° and 1970° C.) were obtained through the use of Wien's "displacement law," in the form

$$E_{\max} = B\theta^5.$$

These measurements, at wave-lengths of 0.656 to 2.172μ , gave a value for C_2 of 1.437 ± 0.004 .

Coblentz's determinations (26) in 1913 were based essentially on 1550° as the melting-point of palladium, although the original temperature determinations were made with thermocouples standardised at 1083° and lower, and used for higher temperatures by extrapolation with assumed corrections. Subsequent standardisation at the palladium point furnished a sound temperature basis. The original value for C_2 , 1.447, has been modified by more recently determined corrections for refractive index and bolometer setting and is now¹ (28) placed at 1.432.

The mean of all the above determinations is about 1.438 ± 0.008 ; or 1.439 ± 0.003 omitting the abnormally high value of Lummer and Pringsheim and the abnormally low value of Holborn and Valentiner. An accuracy of 2° at 1550° (melting-point of palladium) corresponds to 0.0049 in C_2 , or 0.34 per cent. The average deviation of the more recent values from their mean is somewhat less than this.

The possibilities for error in C_2 when determined on the basis of fixed temperatures already standardised by the gas-thermometer are of two kinds: (1) those due to the fixed temperature reproduction, (2) those due to the intensity measurements.

Gold and palladium are the metals commonly used for the fixed melting-points. Gold is easily obtained pure, and accumulated experience has shown that its temperature is readily reproducible within the limits of error of the measurements. The same is not

¹ See article "Radiation, Determination of the Constants," §§ (11), (12), Vol. IV.

true of palladium. It is difficult to purify, and samples of high chemical purity are not readily obtainable.

Impure palladium usually melts higher than pure, as pointed out by Adams (2), and the tendency of impure samples is therefore toward lower values for C_2 . In none of the determinations cited above was the palladium analysed. Only in connection with Day and Sosman's nitrogen-thermometer measurement of the melting-point was its purity determined.

This disadvantage can to a certain extent be overcome by actual comparison of the samples of palladium used with the nitrogen-thermometer sample. This has been done in the cases of Warburg's and Forsythe's measurements. A new platinum-platinrhodium thermocouple, calibrated at the palladium point at the Geophysical Laboratory, agreed satisfactorily with Warburg's temperature scale.

A sample of the nitrogen-thermometer palladium, sent to Dr. Forsythe, proves to have a melting-point averaging within 1° of Forsythe's sample, the range of 15 determinations on each being about 5° . The two samples are therefore identical, as nearly as can be told by this comparison.¹

The other class of errors, those arising from the intensity measurements, includes many small uncertainties that must be taken account of in fundamental work, though often overlooked in past determinations of the constant. An excellent discussion of these errors, particularly with reference to the disappearing-filament type of pyrometer, has been given by Forsythe (49).

We have seen that the average deviation of recent measurements of C_2 from the mean value is of an order of magnitude equivalent to about 2° at 1550° , and that the uncertainties due to the normal variability of the palladium melting-point and to the various sources of error in the optical observations are more than sufficient to account for such a deviation in any one measurement. There appears to be no reason from the thermometric standpoint for adopting any other value for C_2 than the mean value given above, namely, 1.439, nor for adopting any other value for the palladium point than that derived from the nitrogen thermometer,² namely, 1550°C .

The real pressure toward adopting a lower value of C_2 (1.420 to 1.435) arises from the better theoretical agreement between the lower value and the accepted values for Planck's "Quantum" h , the charge of an electron e , the Stefan-Boltzmann radiation constant σ , and other related constants.

¹ Private communication.

² The actual determination is 1549° , but the probabilities favour the existence of a small positive correction of the order of 1° or less to convert constant-volume nitrogen temperatures to thermodynamic.

Whether this is a valid reason for changing the value of C_2 depends to a large extent upon the point of view.

The difference is not large—far too small to be of any industrial importance as yet—but is important enough to deserve considerable further investigation from all points of view, thermometric, theoretical, and radiometric. The investigations of the past few years have been too exclusively occupied with the latter two.

As to the best choice of C_2 in the meanwhile, the history of research furnishes little guidance, for instances can be brought forward in about equal number, on the one hand of good theoretical judgment which disregarded existing data and was afterwards justified by the results of more exact measurement, and on the other hand of apparent discrepancies in experimental results which, though carefully explained away by the experimenter himself, subsequently proved his experimental accuracy to have been better than his judgment.

§ (42) COMBINED THERMAL PROPERTIES AND FIXED TEMPERATURES.—There are two thermal properties which, while not *independently* reproducible with the accuracy desired for thermometry, are nevertheless, when combined with standard fixed temperatures, the main reliance of investigators in the range above 500° . These are (1) the thermal E.M.F. of platinum-group metal thermocouples, among which the Le Chatelier couple, platinum against an alloy of 90 parts platinum and 10 parts rhodium, is pre-eminent, the thermocouples are limited in working range mainly by the melting-temperature of the wires, but also by the contamination of the wires with impurities due to reduction or volatilisation of neighbouring materials; (2) the electrical resistance of pure platinum, limited in its working range to a maximum temperature of 1100°C .

(i.) *Platinum-metal Thermocouples*.—In the preparation and use of thermo-elements Barus made much more extensive and elaborate studies than any one who has followed him. He first investigated a great number of substances, both pure metals and alloys, and measured and tabulated their electromotive forces for different absolute temperatures. From these a couple made from pure platinum and an alloy containing 90 parts platinum and 10 parts of iridium was finally selected for his standard work with the gas-thermometer (5, 8).

It is an unfortunate accident that history has failed to record Barus's name along with that of Le Chatelier (77) in the development of the thermo-element for purposes of high-temperature measurement. There is no question that Barus contributed enormously to our knowledge of the thermo-

electric properties of the different metals and their use, but the 10 per cent iridium alloy which he finally selected proved to be less serviceable than the 10 per cent rhodium alloy developed by Le Chatelier, probably by reason of the greater volatility of the iridium and a consequent slow change in its readings. And so we find the Le Chatelier platinumrhodium thermo-element in use to-day the world over, while the magnificent pioneer work of Barus remains but little known.

The first calibration of the platinum-platinumrhodium couple was made by Holborn and Wien (66, 67) in 1892. They found that the E.M.F. could be represented in terms of temperature by a cubic formula, and that the scale could be reproduced with the aid of melting-points of metals, with an accuracy of 5° , over the range 400° to 1440° .

Holborn and Day (62), though their maximum temperature (1100°) was not as high as that of Holborn and Wien, considerably improved the accuracy of the comparison, and were able to show that the formula $e = -a + bt + ct^2$ holds within 1° over the entire range from 400° to 1100° . Similar comparisons by Harker (51) in 1904 confirmed this empirical relation for the range 400° to 1000° .

Day and Clement's measurements (34) still further improved the accuracy of the measurements, in showing that the quadratic formula is followed from 400° to 1100° , within 0.5° . A certain drift of the deviations was also observed which may indicate that a more complex formula is needed to represent the relation of e and t even more closely than to 0.3° . Data are not yet available for testing this question to a higher degree of accuracy.

The measurements of Day and Sosman were devoted primarily to determining the values of chosen fixed points, using the thermocouple only as a transfer device. The large number of points at small intervals of temperature, which are called for to really test the possible deviation (within 0.3°) from the quadratic formula, is lacking in the data of Day and Sosman because of this concentration of most of the measurements at fixed points. With this limitation (which is equally true of most of the other experimental confirmations of empirical laws in thermometry) the data of Day and Sosman furnish a good test of the quadratic equation, since the substitution of a platinumrhodium alloy in place of platinumiridium as the bulb material considerably increased the attainable precision with thermocouples, removing as it did the serious source of error due to contamination of the couples with iridium. The data show that the quadratic formula represents the mode of variation of e with t over the range from 300° to 1100° with an accuracy of 0.3° , while a similar formula

with different constants will cover the range 1000° to 1550° within 1° . A cubic equation can be made to fit all the points from 300° to 1550° with a deviation of a little over 1° .

(ii.) *Electrical Resistance of Platinum Wire.*—The only direct calibration of a platinum-resistance thermometer by reference to a gas-thermometer that has ever been made in the range above 500° is the comparison by Harker (51) in 1904. Using a constant-volume nitrogen thermometer with porcelain bulbs, Harker showed that between 400° and 1000° the quadratic formula for the platinum resistance yielded temperatures that were within 1° of the gas-thermometer at the lower temperatures, but deviated by more than the probable error in the upper part of the range, the difference reaching a maximum of 6.3° .

In the ultimate analysis, then, confidence in the platinum-resistance thermometer above 500° depends on the degree of accuracy with which it can interpolate the melting-points of antimony and silver between the two base-points, 444.55° (sulphur) and 1063° (gold). A really exact standardisation, having a precision comparable with that of which both the gas-thermometer and platinum-resistance thermometer are now capable, has yet to be made.

(iii.) *Interpolated Fixed Points.*—As already pointed out in preceding sections, determinations of fixed temperatures may be roughly divided into four classes: (1) those determined directly by immersion of the gas-thermometer in the constant-temperature system (sulphur vapour, for example); (2) those determined indirectly by transferring the temperature from gas-thermometer to fixed point by means of an intermediary transfer device; (3) those determined by first establishing the law of variation of a secondary thermometer (thermo-element, for example) and then using this thermometer to interpolate the fixed points; (4) those "secondary interpolations" made by calibrating a secondary thermometer at several known fixed points determined by methods (1), (2), or (3), and then using it for further interpolation.

"Primary interpolations" of class (3) were made by Holborn and Wien, Holborn and Day, and Day, Clement, and Sosman by means of thermocouples.

Several "secondary interpolations" of class (4) (Heycock and Neville, Waidner and Burgess) have been made with platinum-resistance thermometers. These were originally made as *extrapolations* of the Callendar formula over the range from 500° to 1100° , an extrapolation more than equal to the range for which the law had been established. The melting-point data so obtained are often quoted as independent determinations of the points, side by side with gas-thermometer determina-

tions. Strictly speaking, they are not determinations at all, but merely hopeful estimates. Such an extrapolation of an empirical law to cover an additional range more than equal to that for which it has been established is justifiable only as a temporary measure. That it does sometimes succeed is shown by the unexpectedly close agreement between the melting-points extrapolated with the platinum-resistance thermometer and the actual determinations made later with the gas-thermometer. Usually the attempt has failed, as in the case of platinum resistance below 0° , and of the thermo-element above 1100° , but the erroneous results have been quickly forgotten, and have done harm only by producing temporary confusion. The original comparisons have permanent value, furthermore, when the extension of the gas-thermometer scale establishes the true law of variation.

A number of primary and secondary interpolated melting-points are shown in Table 13, compared with direct or indirect gas-thermometer determinations of the same points.

calibration at three points (such as the melting-points of zinc, gold, and palladium), and the use of a standard table such as that of Adams (1), nitrogen scale temperatures can be measured within 0.3° at 500° and 3° at 1500° .

(ii.) *Platinum-resistance Thermometry.*—Nitrogen scale temperatures between 500° and 1100° can be measured with a platinum-resistance thermometer made of pure platinum and standardised at the sulphur boiling-point and the gold melting-point within 0.3° at 500° and 1° at 1000° .

(iii.) *Optical and Radiation Thermometry.*—By calibration at the melting-points of gold and palladium, nitrogen scale temperatures can be measured optically or by total radiation, when the various correction factors for absorption, etc., are taken into account, within 2° at 1000° and 5° at 1600° .

(iv.) *Fixed Points.*—The following fixed points may be used to establish and maintain the temperature scale from 500° to 1600° , and are known on the centigrade thermodynamic scale with the accuracy indicated.

TABLE 13

INTERPOLATED VALUES OF FIXED POINTS IN THE RANGE 500° TO 1600° COMPARED WITH GAS-THERMOMETER DETERMINATIONS

Author.	Date.	M.P. Antimony.	M.P. Aluminium.	M.P. Silver.	M.P. Gold.	M.P. Copper.	Basis.
<i>Direct or Indirect Gas-thermometer Determinations.</i>							
Jaquered and Perrot .	1905	1067.4	..	{ Constant-volume N, O, CO, and CO ₂ . Constant-volume nitrogen.
Day, Sosman, and Allen	1910-12	630.0	..	960.0	1062.4	1082.6	
<i>Primary Interpolations.</i>							
Holborn and Wien .	1892	968	1072	1082	{ Pt : PtRh couple and constant - volume air thermometer. Pt : Pt Rh couple and constant - volume nitrogen thermometer.
Holborn and Day .	1900	630.6	..	961	1064	1084	
Day and Sosman .	1911	..	658.7	
<i>Secondary Interpolations.</i>							
Heycock and Neville .	1895	630.2	655.3	962	1063.7	..	{ Pt res. thermometer be- tween 444.55° and 1083.0°.
Waidner and Burgess .	1910	630.7	658.0	960.9	

§ (43) SUMMARY FOR THE RANGE 500° TO 1600° . (i.) *Thermoelectric Thermometry.*—The best secondary thermometer for use in the range 500° to 1600° is the platinum:platin-rhodium thermo-element. The E.M.F. of the couple can be represented in terms of the constant-volume nitrogen scale by a quadratic equation over limited parts of the range (300° to 1100° and 1000° to 1550°) with an accuracy of within 0.3° in the lower part of the range and within 2° at 1500° . A cubic equation will represent all temperatures from 300° to 1550° with somewhat less accuracy. By

It is assumed that the substances used are the purest obtainable commercially.

Melting-point of antimony . . .	$630 \pm 0.5^{\circ}$
„ „ aluminium . . .	$659 \pm 0.5^{\circ}$
„ „ silver . . .	$960 \pm 0.5^{\circ}$
„ „ gold . . .	$1063 \pm 0.5^{\circ}$
„ „ copper . . .	$1083 \pm 1^{\circ}$
„ „ diopside (CaMgSi ₂ O ₆) . . .	$1391 \pm 2^{\circ}$
„ „ palladium . . .	$1550 \pm 3^{\circ}$

Some of these substances are now obtainable as certified standards for thermometric calibration (for example, aluminium from the Bureau of Standards of the United States).

(v.) *Thermodynamic Scale*.—The corrections to convert readings on the constant-volume gas scales to the thermodynamic scale at 1000° and higher are very uncertain. The correction to the constant-volume nitrogen scale at initial pressure 500 mm. is probably of the order of magnitude of +0.5° or less at 1200°.

IX. THE SOURCES OF ERROR IN GAS THERMOMETRY

§ (44) *CONSTANT-PRESSURE THERMOMETER*.—The development of the constant-pressure gas-thermometer has remained almost wholly in the hands of Callendar and his associates. From its inception in 1886 to the last important publication in 1914 no serious attempt has been made to extend the use of the instrument to the higher temperatures (above the sulphur boiling-point). For this reason, perhaps, the sources of error in this system of procedure have remained undeveloped and cannot be

permanent change in the volume of the bulb after each exposure at the higher temperatures; (2) changes and uncertainty in the expansion coefficient of the bulb material (18) (chiefly glass and porcelain); (3) inexact knowledge of the expansion coefficient of mercury through an adequate temperature range. These errors are of a kind which can be greatly reduced in magnitude by a judicious selection of bulb material and careful study, and the constant-pressure gas-thermometer may yet prove to be a most valuable instrument for the determination of standard high temperatures. At the moment, however, one must regard it as an untried instrument in the region where further work is mainly needed (above 1200°) and no experience is available through which to forecast its behaviour there.

§ (45) *CONSTANT-VOLUME THERMOMETER*.—The sources of error in the constant-volume gas-thermometer, on the contrary, are now

TABLE 14
CONSTANT CORRECTIONS TO THE CONSTANT-VOLUME GAS-THERMOMETER (DEGREES)

Temp. ° C.	Unheated Space Ratio assumed $v/V_0=0.01$.		Thermal Expansion.						Elastic Expansion assumed $=10^{-7}$ per mm.	
			Pt-Ir.		Glass 59 ^{III} .		Fused Silica.			
	Δ.	Δ'.	Δ.	Δ'.	Δ.	Δ'.	Δ.	Δ'.	Δ.	Δ'.
- 270	- 0.03	+ 3.4	- 0.00	+0.04
- 200	- 0.50	+ 2.1	- 0.01	+0.02
- 191	- 0.54	+ 1.9	- 0.38	+ 1.4	- 0.22	+ 0.78	+ 0.01	- 0.04	- 0.01	+0.02
- 100	- 0.59	+ 0.69	- 0.01	+0.01
0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
+ 100	+ 1.3	0.00	+ 0.92	0.00	+ 0.61	0.00	+ 0.06	0.00	+ 0.01	0.00
+ 200	+ 3.3	+ 0.69	+ 2.4	+ 0.54	+ 1.7	+ 0.38	+ 0.15	+ 0.03	+ 0.03	+ 0.01
+ 500	+ 13	+ 6.9	+ 10	+ 5.7	+ 7.3	+ 4.0	+ 0.63	+ 0.32	+ 0.14	+ 0.07
+ 1000	+ 44	+ 31	+ 37	+ 27	+ 2.1	+ 1.5	+ 0.47	+ 0.33
+ 1500	+ 91	+ 72	+ 82	+ 68	+ 0.98	+ 0.77

examined with the same sharp scrutiny which may now be applied to the sources of error in the constant-volume instrument. In principle the apparatus is sound, and when judged from theoretical considerations alone has been accorded the preference by several writers on the subject. It has also been stoutly defended by Callendar on several explicit grounds: (1) both the apparatus and the calculation are simple; (2) the internal pressure upon the bulb does not increase with the temperature to be measured; (3) the accuracy is limited only by the precision with which weighings can be made.

Over against this may be set the fact that results obtained with the instrument have not been satisfactorily concordant, even though observations with it have been confined to a short range of easily accessible temperatures. The sources of error thus far recognised by Callendar and his active coadjutor Eumorfopoulos are mainly three: (1) a

so well known that no more than a brief review of them is needed here. In the comprehensive treatment of gas thermometry by Henning (56) three primary correction factors in which lie sources of error have been emphasised and their magnitude tabulated for various temperatures. The data are contained in Table 14, which will serve to show the magnitude to which these correction factors attain in common practice; the errors arising therefrom are in most cases naturally a small fraction of the correction stated. The corrections marked Δ in the table are on the assumption that the pressure-coefficient of the gas, β , is independently known; those marked Δ' are on the assumption that β has been determined in the same apparatus.

Of these magnitudes it should be stated that the first, v/V_0 , the ratio of the volume of the connecting tube between bulb and manometer to that of the bulb, was reduced by Day and Sosman to about one-sixth

of the value assumed by Henning in the above computation, and its temperature and volume are determinable with such accuracy that this can hardly be accounted a major source of error now.

The expansion coefficient of the bulb material will always be a factor requiring precise determination. To determine the expansion coefficient of a stable and well-defined solid to a few parts in a thousand even over a very great temperature range offers no difficulty to-day, but the solids which are chosen for their refractory quality or for their impermeability to certain gases may be neither stable nor well-defined. Witness, for example, the materials cited in the above table which are those now most commonly used for high-temperature gas-thermometry. Silica glass, and indeed all glasses, are in unstable equilibrium in which normal molecular forces are held in check by extreme viscosity. Diminish this viscosity by exposure to a sufficiently high temperature and the instability will appear as a more or less complete change of physical state. Silica glass, for example, begins to crystallise at an appreciable rate at about 1100°, while at higher temperatures the change becomes rapid. More complicated glasses such as Jena 59^{III} develop various crystalline compounds when heated. Platiniridium is a stable alloy at low temperatures but in the higher ranges loses iridium and may take on iron or silicon if present in a reducing atmosphere. With adequate protection against these contingencies, that is to say, in an appropriate atmosphere and temperature range, each of these substances has a determinable expansion coefficient through which no error of appreciable magnitude need enter the temperature determination. The effort to stretch the range of measurements with a particular bulb to temperatures within the region where the material becomes measurably weak or incipient crystallisation occurs (in glasses) or a finely crystalline alloy becomes coarsely crystalline, brings uncertain expansion, permanent changes of the ice-point, deformation, and like uncertainties impossible to measure and difficult to appraise.

The elastic expansion of the bulb under change of internal pressure need give no further concern. Theoretically it does not arise in the constant-pressure thermometer, though Callendar's observations (with glass bulbs) appear not to have been entirely free from the effects of volume-changes at any time. Practically it may be completely avoided in the constant-volume thermometer by enclosing the bulb in a bomb in which the pressure outside the bulb is regulated to correspond to the pressure within, as was done by Day and Sosman. The principal uncertainties met with in constant-volume gas thermometry

to-day, assuming that the bulb has been chosen appropriately for the temperature range to be measured and full advantage is taken of existing experience, are not sources of error properly inherent in the gas-thermometer system. They are (1) the temperature distribution about the bulb, *i.e.* the *uniformity of temperature* in the space to be measured; and (2) the uniformity of temperature distribution about the mercury manometers. After a long experience with high-temperature measurement it is our impression that a space sufficient to enclose a 200 c.c. bulb, *all* of which has a temperature of 1500° C. $\pm 5^\circ$, has perhaps never been available to a student of gas-thermometry. How then shall we measure such a temperature with this precision? Holborn and Valentiner record the fact that in their attempt to reach 1600° with a bulb of pure iridium, differences of temperature were observed on the bulb surface amounting to as much as 60°. How much greater than this the temperature variations in the zone of measurement might have been without the integrating effect of the bulb wall of metallic iridium it is impossible to say. The first necessity in the attainment of precise temperature definition at 1500°, which happens to be the temperature region in which most of the recent gas-thermometry has been carried out, is a suitable space *uniformly* heated to 1500°. Given this, and the errors discussed above become relatively insignificant magnitudes.

In the same sense, future gas-thermometry must place the long columns of mercury forming the manometer in a thermostat where the temperature can be properly controlled. It is no longer necessary at the highest temperatures that the gas pressure within the bulb should not exceed one atmosphere lest the bulb become strained and the "constant volume" be jeopardised. Two or three times this pressure may be used equally well and a corresponding increase of sensitiveness attained, but the increased length of the measuring column of mercury must not introduce errors through uncertainties in the mercury temperature. A further advantage in simplified technique would also be attained if a closed-tube manometer were substituted for the more usual open-tube manometer; in many cases this has not been done hitherto, chiefly because it would have added the barometric height to the already long mercury column and the difficulty of temperature control of the column would have been increased.

The relative magnitude of the accidental sources of error in a typical set of measurements with the constant-volume gas-thermometer are shown in Table 15, compiled by Day and Sosman in connection with their work on the nitrogen thermometer in the range 500° to 1550°.

TABLE 15

EXAMPLE SHOWING ACCIDENTAL ERRORS IN GAS-THERMOMETRY. ESTIMATED ERRORS OF A CONSTANT-VOLUME NITROGEN-THERMOMETER AT INITIAL PRESSURE OF ABOUT 200 MM. MERCURY (37)

Bulb material : 80 platinum, 20 rhodium.
 Volume of bulb : $V_0 = 206$ c.c.
 Volume of unheated space : $v_1 = 0.31$ c.c.
 Ratio $v_1/V_0 = 0.0015$.
 Furnace : electrically heated air-bath.
 Manometer : open type. Barometer read separately.
 Pressure-coefficient of gas and expansion-coefficient of bulb assumed known.
 Temperature transferred to fixed points by platinum : platinum-rhodium thermocouples.

Quantity Affected.	Source of Error.	Amount of Error.		Effect on t .	
		At 400°.	At 1500°.	At 400°.	At 1500°.
(A) Temperature of gas	Temperature differences over bulb surface	2 mv.	5 mv.	$\pm 0.2^\circ$	$\pm 0.4^\circ$
	Variability	0	1 "	0	± 0.1
	Reference point	0.02 mm.	0.02 mm.	± 0.04	± 0.15
(B) p_0	Manometer setting	0.02 "	0.02 "	± 0.04	± 0.15
	Scale corrections	0.01 "	0.01 "	± 0.02	± 0.07
	Temperature of mercury	0.03 "	0.03 "	± 0.06	± 0.23
	Barometer setting	0.03 "	0.03 "	± 0.06	± 0.23
	Temperature of barometer	0.03 "	0.03 "	± 0.06	± 0.23
(B) p	Permanent variations in p_0	0	0 to .05 "	0	0 to ± 0.3
	Reference point	0.02 "	0.02 "	± 0.02	0
	Manometer setting	0.02 "	0.02 "	± 0.02	0
	Scale corrections	0.02 "	0.02 "	± 0.02	0
	Temperature of mercury	0.07 "	0.20 "	± 0.07	± 0.05
(C) E.M.F.	Barometer setting	0.03 "	0.03 "	± 0.03	± 0.01
	Barometer temperature	0.03 "	0.03 "	± 0.03	± 0.01
	Unheated space, v_1	0.020 c.c.	0.020 c.c.	± 0.07	± 0.5
	Unheated space, t_1	0.5-50°	0.5-100°	± 0.01	± 0.1
	Instrumental corrections	1 mv.	2 mv.	± 0.1	± 0.2
(D) Fixed points	Contamination	0	0.12 mv.	0	0 to +1.0
	Integration over bulb	5 mv.	12 mv.	± 0.5	± 1.0
	Instrumental corrections	1 mv.	2 mv.	± 0.1	± 0.2
	Contamination	0	0.10 mv.	0	0 to -1.0
	Variation in given charge	Specific, 1-10 mv.		Specific, 0.1 to 1.0	
	Variation between different charges	Specific, 1-20 "		Specific, 0.1 to 2.0	

In conclusion, we wish to record our indebtedness to Messrs. L. H. Adams, E. Buckingham, W. W. Coblentz, E. F. Mueller, C. W. Waidner, and W. P. White for suggestions concerning various parts of this article.

REFERENCES

1. L. H. Adams, *J. Am. Chem. Soc.*, 1914, xxxvi. 65-72.
2. L. H. Adams, *Am. Inst. Min. Met. Eng.*, 1920, Pyrometry Vol., pp. 59, 60.
3. L. H. Adams and J. Johnston, *Am. J. Sci.*, 1912, xxxiii. 534-545; *J. Wash. Acad. Sci.*, 1912, ii. 275-284.
4. E. C. Baly, *Phil. Mag.*, 1900, xlix. 517-529.
5. C. Barus, *U.S. Geol. Survey Bull.*, 1889, liv.
6. C. Barus, *Phys. Rev.*, 1892, ii. 295-316.
7. C. Barus, *Die physikalische Behandlung und die Messung hoher Temperaturen*, Leipzig, 1892.
8. C. Barus, *Am. J. Sci.* (3), 1894, xlviii. 332-337.
9. Ed. Becquerel, *Ann. Chim. et Phys.* (3), 1863, lxxviii. 49-143.
10. D. Berthelot, *Compt. Rend.*, 1895, cxx. 831-834.
11. D. Berthelot, *Compt. Rend.*, 1898, cxxvi. 410-412.
12. D. Berthelot, *Compt. Rend.*, 1898, cxxvi. 473-476.
13. D. Berthelot, *Trav. et Mém. Bur. Int.*, 1907, xiii. 113 pp.
14. E. Buckingham, *Bureau of Standards Bull.*, 1907, iii. 237-293 (Sci. Paper, 57).
15. E. Buckingham, *Bureau of Standards Bull.*, 1910, vi. 409-429.
16. H. L. Callendar, *Phil. Trans.*, 1887, A, clxxviii. 161-230, Pl. 11-13.
17. H. L. Callendar, *Phil. Mag.*, 1903, v. 48.
18. H. L. Callendar, *Proc. Roy. Soc.*, 1908, A, lxxxi. 363-366.
19. H. L. Callendar and E. H. Griffiths, *Phil. Trans.*, 1891, A, clxxii. 119-157.
20. H. L. Callendar and H. Moss, *Proc. Roy. Soc.*, 1910, A, lxxxiii. 106-108.
21. P. Chappuis, *Trav. et Mém. Bur. Int.*, 1888, vi. 125+187 pp., Pl. 1.
22. P. Chappuis, *Trav. et Mém. Bur. Int.*, 1907, xiii. 66 pp.
23. P. Chappuis, *Trav. et Mém. Bur. Int.*, 1917, xvi. 44 pp.
24. P. Chappuis and J. A. Harker, *Trav. et Mém. Bur. Int.*, 1902, xii. 89 pp.
25. P. Chappuis, *Trav. et Mém. Bur. Int.*, 1902, xii. (Conférence Générale, 1895, p. 20).
26. W. W. Coblentz, *Bureau of Standards Bull.*, 1913, ix. 283-325.

27. W. W. Coblentz, *Bureau of Standards Bull.*, 1914, x, 1-77; 1916, xlii, 459-477.
28. W. W. Coblentz, *Bureau of Standards Sci. Pap.*, 1921, xvii, 7-48; No. 406.
29. W. W. Coblentz and W. B. Emerson, *Bureau of Standards Bull.*, 1916, xii, 503-551.
30. W. W. Coblentz, *Bureau of Standards Bull.*, 1916, xii, 553-582.
31. W. W. Coblentz, *Proc. Nat. Acad. Sci.*, 1917, iii, 504-505.
32. J. M. Crafts, *Nature*, 1882, xxvi, 466.
33. J. M. Crafts, *J. Chim. Phys.*, 1913, xi, 429-477.
34. A. L. Day and J. K. Clement, *Am. J. Sci.*, 1908, xxvi, 405-463.
35. A. L. Day and R. B. Sosman, *Am. J. Sci.*, 1912, xxxiii, 517-533; *J. Wash. Acad. Sci.*, 1912, ii, 167-176; *Ann. Phys.*, 1912, xxxviii, 849-869.
36. A. L. Day and R. B. Sosman, *J. Physique*, 1912, (5), ii, 727-749, 831-844, 899-911.
37. A. L. Day, R. B. Sosman, and E. T. Allen, *Am. J. Sci.*, 1910, (4), xxix, 93-161.
38. A. L. Day, R. B. Sosman, and E. T. Allen, *Carnegie Inst. Publ. No.* 157, 1911.
39. St. Claire-Deville and Troost, *Compt. Rend.*, 1857, xlv, 821-825; 1859, xlix, 239-242; *Ann. Chim. et Phys.* (3), 1860, lviii, 257-299.
40. St. Claire-Deville and Troost, *Compt. Rend.*, 1863, lvii, 897-902; 1864, lix, 162-170.
41. J. Dewar, *Proc. Roy. Soc.*, 1901, lxxviii, 44-54.
42. J. Dewar, *Roy. Soc. Proc.*, 1905, lxxvi, 316-325.
43. H. C. Dickinson and E. F. Mueller, *Bureau of Standards Bull.*, 1907, iii, 641-661.
44. H. C. Dickinson and E. F. Mueller, *J. Wash. Acad. Sci.*, 1912, ii, 176-180.
45. Erhard and Schertel, *Jahrb. f. Berg- u. Hüttenwesen im Sachsen*, 1879, 154.
46. T. Estreicher, *Phil. Mag.*, 1895, xl, 454-463.
47. N. Eumorfopoulos, *Roy. Soc. Proc.*, 1908, A, xxxi, 339-362.
48. N. Eumorfopoulos, *Roy. Soc. Proc.*, 1914, A, xc, 189-203.
49. W. E. Forsythe, *Am. Inst. Min. Met. Eng.*, 1920, Pyrometry Vol., 291-323.
50. E. H. Griffiths, *Phil. Trans.*, 1893, A, clxxiv, 430.
51. J. A. Harker, *Phil. Trans.*, 1904, A, cciii, 343-384.
52. J. A. Harker, *Roy. Soc. Proc.*, 1906, lxxviii, 225-240.
53. F. Henning, *Ann. d. Physik*, 1913, xl, 635-667.
54. F. Henning, *Zeits. Instrumentenk.*, 1914, xxxiv, 116.
55. F. Henning, *Ann. d. Physik*, 1914, xliii, 282-294.
56. F. Henning, *Die Grundlagen, Methoden, und Ergebnisse der Temperaturmessung*, Braunschweig, 1915.
57. C. T. Heycock and F. H. Neville, *J. Chem. Soc. (London)*, 1895, lxvii, 160-199.
58. Hoffmann and Meissner, *Zeits. Instrumentenk.*, 1912, xxxii, 201; 1913, xxxiii, 95, 157.
59. F. Hoffmann and W. Meissner, *Ann. d. Physik*, 1919, lx, 201-232.
60. L. Holborn, *Ann. d. Physik*, 1901, vi, 242-258.
61. L. Holborn and A. L. Day, *Wied. Ann.*, 1899, lxviii, 817-852; *Am. J. Sci.* (4), 1899, viii, 165-193.
62. L. Holborn and A. L. Day, *Ann. d. Physik*, 1900, ii, 505-545; *Am. J. Sci.* (4), 1900, x, 171-206.
63. L. Holborn and F. Henning, *Ann. d. Physik*, 1908, xxvi, 833-883.
64. L. Holborn and F. Henning, *Ann. d. Physik*, 1911, xxxv, 761-774.
65. L. Holborn and S. Valentiner, *Sitzungsb. Berlin Akad.*, 1906, 811-817; *Ann. d. Physik*, 1907, xxii, 1-48.
66. L. Holborn and W. Wien, *Wied. Ann.*, 1892, xlvii, 107-134.
67. L. Holborn and W. Wien, *Wied. Ann.*, 1895, lvi, 360-396.
68. L. Holborn and W. Wien, *Ann. d. Physik*, 1896, lix, 213-228.
69. G. H. Hoxton, *Phys. Rev.*, 1919, xiii, 438-479.
70. E. P. Hyde, F. E. Cady, and W. E. Forsythe, *Astrophys. J.*, 1915, xlii, 294-304.
71. E. P. Hyde and W. E. Forsythe, *Phys. Rev.*, 1920, xv, 540.
72. A. Jaquero and F. L. Perrot, *Arch. Sci. Phys. Nat. Genève* (4), 1905, xx, 28-58, 128-158, 454-455, 506-529.
73. A. Jaquero and E. Wassmer, *J. Chim. Phys.*, 1904, ii, 52-78.
74. E. Kaspar, Diss., Marburg, 1913.
75. F. G. Keyes, *J. Am. Chem. Soc.*, 1920, xlii, 54-60.
76. A. Ladenburg and C. Krügel, *Ber. Deut. Chem. Ges.*, 1899, xxxii, 1818-1822.
77. H. Le Chatelier, *Bull. Soc. Chim.*, 1887, xlvii, 2; *Journ. d. Physique*, 1887, vi, 23.
78. O. Lummer and E. Pringsheim, *Verh. Deut. Phys. Ges.*, 1899, i, 23-41.
79. O. Lummer and E. Pringsheim, *Verh. Deut. Phys. Ges.*, 1901, iii, 36-46; *Zeits. Instrumentenk.*, 1901, xxi, 116-120.
80. W. Makower and H. R. Noble, *Roy. Soc. Proc.*, 1903, lxxii, 379-385.
81. B. Mellink, *Versl. Ak. Amsterdam*, 1902, 566-572; Leiden Comm. No. 77.
82. B. Mellink, *Versl. Ak. Amsterdam*, 1904, 212-233; Leiden Comm. No. 93.
83. C. E. Mendenhall, *Phys. Rev.* (2), 1917, x, 522.
84. R. A. Millikan, *Proc. Nat. Acad. Sci.*, 1917, iii, 231-236.
85. W. Nernst and H. von Wartenburg, *Verh. Deut. Phys. Ges.*, 1906, viii, 48-58.
86. K. Olzewski, *Nature*, 1896, liv, 377-378.
87. H. Kamerlingh Onnes, *Versl. Ak. Amsterdam*, 1907, 501-504; Leiden Comm. No. 102b.
88. H. Kamerlingh Onnes and M. Boudin, *Versl. Ak. Amsterdam*, 1900, 224-241; Leiden Comm. No. 60.
89. H. Kamerlingh Onnes and C. Braak, *Versl. Ak. Amsterdam*, 1907, 668-677; Leiden Comm. No. 97b.
90. H. Kamerlingh Onnes and C. Braak, *Versl. Ak. Amsterdam*, 1908, 743-744; Leiden Comm. No. 102d.
91. H. Kamerlingh Onnes and C. Braak, *Versl. Ak. Amsterdam*, 1907, 427-430; Leiden Comm. No. 101b.
92. H. Kamerlingh Onnes and C. Braak, *Versl. Ak. Amsterdam*, 1908, 86-93; Leiden Comm. No. 107a.
93. H. Kamerlingh Onnes, C. Braak, and J. Clay, *Versl. Ak. Amsterdam*, 1907, 420-426; Leiden Comm. No. 101a.
94. H. Kamerlingh Onnes and J. Clay, *Versl. Ak. Amsterdam*, 1906, 160-165; Leiden Comm. No. 95c.
95. H. Kamerlingh Onnes and J. Clay, *Versl. Ak. Amsterdam*, 1906, 165-168; Leiden Comm. No. 95d.
96. H. Kamerlingh Onnes and J. Clay, *Versl. Ak. Amsterdam*, 1907, 169-177; Leiden Comm. No. 99c.
97. H. Kamerlingh Onnes and J. Clay, *Versl. Ak. Amsterdam*, 1908, 94-95; Leiden Comm. No. 107b.
98. H. Kamerlingh Onnes and C. A. Crommelin, *Versl. Ak. Amsterdam*, 1906, 133-151, 365-367; Leiden Comm. No. 95a, 95f.
99. H. Kamerlingh Onnes and G. Holst, *Versl. Ak. Amsterdam*, 1914, 175-182; Leiden Comm. No. 411a.
100. M. Planck, *Verh. Deut. Phys. Ges.*, 1900, ii, 202-204.
101. Pouillet, *Comptes Rendus*, 1836, iii, 782-790.
102. Jas. Prinsep, *Roy. Soc. Phil. Trans.*, 1828, 79-95; *Ann. Chim. et Phys.* (2), 1829, xli, 247.
103. Regnault, *Mém. Acad. Sci. Paris*, 1847, xxi, 168.
104. Regnault, *Ann. Chim. et Phys.* (3), 1861, lxiii, 39-56.
105. T. W. Richards, *Zeits. Phys. Chem.*, 1898, xxvi, 690.
106. T. W. Richards and R. C. Wells, *Zeits. Phys. Chem.*, 1903, xliii, 465.
107. T. W. Richards and R. C. Wells, *Zeits. Phys. Chem.*, 1906, lvi, 348-361.
108. T. W. Richards and F. Wrede, *Am. Acad. Proc.*, 1908, xliii, 341-350; *Zeits. Phys. Chem.*, 1908, lxi, 313-320.
109. J. Rose-Innes, *Phil. Mag.*, 1901, ii, 130.
110. A. Stock and C. Nielsen, *Ber. Deut. Chem. Ges.*, 1906, xxxix, 2066-2069.
111. R. C. Tolman, *Phys. Rev.*, 1917, ix, 237-253.
112. M. W. Travers and C. J. Fox, *Roy. Soc. Proc.*, 1903, lxxii, 386-391.
113. M. W. Travers and A. G. C. Gwyer, *Roy. Soc. Proc.*, 1905, lxxiv, 528-538; *Zeits. Phys. Chem.*, 1905, lii, 437-448.
114. M. W. Travers, G. Senter, and A. Jaquero, *Phil. Trans.*, 1903, A, cc, 105-180; *Zeits. Phys. Chem.*, 1903, xlv, 385-415, 416-434, 435-460.

115. S. Valentiner, *Ann. d. Physik* (4), 1910, xxxi. 275-311.
 116. S. Valentiner, *Ann. d. Physik*, 1912, xxxix. 489-492.
 117. J. Violle, *Comptes Rendus*, 1877, lxxxv. 543-546.
 118. J. Violle, *Comptes Rendus*, 1878, lxxxvii. 981-984.
 119. J. Violle, *Comptes Rendus*, 1879, lxxxix. 702-703.
 120. J. Violle, *Comptes Rendus*, 1882, xciv. 720-722.
 121. C. W. Waidner and H. C. Dickinson, *Bureau of Standards Bull.*, 1907, iii. 663-728.
 122. C. W. Waidner and G. K. Burgess, *Bureau of Standards Bull.*, 1910, vi. 149-230.
 123. C. W. Waidner and G. K. Burgess, *Bureau of Standards Bull.*, 1911, vii. 1-9.
 124. C. W. Waidner and F. Mallory, *Phys. Rev.*, 1899, viii. 193-236; *Phil. Mag.*, 1899, xlviii. 1-45.
 125. E. Warburg, *Zeits. Instrumentenk.*, 1916, xxxvi. 20-21.
 126. E. Warburg, G. Leithaeuser, E. Hupka, C. Mueller, *Ann. d. Physik*, 1913, xl. 609-634.
 127. S. v. Wroblewski, *Sitzungsber. Wien. Akad.*, 1888, xcvi. 1321-1379.

A. L. D.

R. B. S.



3 0112 106067892

UNIVERSITY OF ILLINOIS LIBRARY